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FLAMMABILITY CHARACTERISTICS OF DISTILLATE FUELS

INTERIM REPORT
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By

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The objectives of this effort were to develop basic information on flammability characteristics of diesel and turbine engine fuels and to provide useful criteria for prediction of fuel fire dynamics in a hostile environment due to armor/fuel cell penetration. Four selected representative fuels (DF-1, DF-2, JP-8, and a high aromatic content light cycle oil) were extensively characterized for important physicochemical properties. The fuels were chemically analyzed by gas chromatography (GC)/mass spectrometry (MS), and proton and carbon-13 nuclear magnetic resonance. Thermophysical properties of the fuels were determined by differential scanning calorimetry and steady-state hot wire thermal conductivity cell.

Idealized blends containing about five pure hydrocarbon components were formulated based on chemical analysis of the real fuels. The vapor phase composition of the fuels pyrolyzed under various

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inert and oxidizing conditions were determined by pyrolysis/GC/MS. Experiments were also conducted in a high-temperature flow reactor to measure nonequilibrium vapor compositions due to oxidative and thermal decompositions of the fuels. Preliminary experiments were conducted to address simulated events within the fuel cell just after ballistic/plasma penetration. Results of experimental work are discussed and recommendations made for future studies.

FOREWORD

This work was conducted at the Belvoir Fuels and Lubricants Research Facility (SwRI) located at Southwest Research Institute (SwRI), San Antonio, TX under Contract No. DAAK70-85-C-0007 during the period February 1985 through June 1987. The work was funded by the U.S. Army Belvoir Research, Development and Engineering Center, Ft. Belvoir, VA, with Mr. F.W. Schaekel (STRBE-VF), as the Contracting Officer's Representative and Mr. M.E. LePera, Chief of Fuels and Lubricants Division (STRBE-VF), as the project technical monitor.

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I. INTRODUCTION

The U.S. Army has a need for a diesel fuel that would perform satisfactorily in diesel-powered combat vehicles, but would self-extinguish in case of ignition by ballistic penetration or other undesirable ignition source. The main thrust for this investigation was based on experience which indicated that fuel fires can be a major cause of ground vehicle and personnel losses. If catastrophic fuel fires could be eliminated, the possibility for personnel survival would increase, and chances of repair or salvage of vehicles would be improved. Thus, cost effectiveness would be realized not only in reduced key personnel losses, but also through improved supply of critical tactical equipment in an area where resupply may be difficult.

II. BACKGROUND

A Short-Term Advisory Services (STAS) team in 1984 examined several approaches to fuel fire reduction.(1)* The STAS team recommended that fuel cooling/fuel flash point modification and compartment deluge with halon held high potential for development and deployment. It was also recommended that with fuel cooling and suitable fuel system modifications, conventional antimisting agent (AM-1) may have some potential for reducing aerosol formation.

A series of full-scale ballistic tests with 90-mm HEAT were conducted by Belvoir Fuels and Lubricants Research Facility (BFLRF) (SwRI) (2) on an M-113 APC to evaluate how fire vulnerability is affected by some of the STAS-recommended approaches to diesel fuel in armored vehicle fuel cells. The tests considered four variables: fuel temperature, air availability, antimisting additive concentration, and halon fire suppression. The results of that investigation can be summarized as follows:

1. Cooling the fuel, a 61°C flashpoint DF-2, to 2°C did not reduce fire vulnerability.

2. Fuel cooling, accompanied by a high concentration of antimisting agent (0.35 wt% AM-1), has potential for preventing pool fire and reducing the mist fireball.

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

3. The antimist additive was not effective in reducing pool fires at bulk fluid temperatures near or above base fuel flash point.

4. The Halon 1301 fire suppression system can effectively control fires resulting from neat fuel or fuel containing antimist agent provided proper nozzle orientation and dispersal timing are accomplished.

5. Air availability in the personnel compartment or quenching of fires due to heat sinks reduces duration and size of fires, thus indicating that a design modification could possibly be effective in reducing pool burning.

Examination of the high-speed movie records of these tests showed that the fuel spray emanating from the fuel tank ruptured by HEAT rounds is always ignited regardless of the bulk fuel temperature. This burning fuel spray (mist fireball) would descend on the fuel pool formed on the floor of the vehicle. The size and duration of the mist-fireball and the net exchange rate of heat from it to the fuel spill determined the propagation of the pool fire. Thus, the dynamic heat balance in the fuel cell between the liquid and the energetic round influences the size and duration of the fireball. Other factors that play an important role in the mist-fireball development are the materials of construction of the armor and the fuel cell, the penetration mechanics, and hydrodynamics of fuel. The rate of heat exchange between the mist fireball and the spilled fuel generally determined if the pool fire will propagate.

III. OBJECTIVE AND APPROACH

The objective of this research effort was to develop basic information on fuel ignition and flammability propagation of diesel and turbine fuels. This information will provide useful criteria for prediction of fire safety from the development of fuel fire hazard in a hostile environment due to armor/fuel cell penetration.

Several diesel/turbine engine fuels of interest to the U.S. Army were investigated for their chemical compositions, distillation properties, thermophysical properties, and their flash points.

An apparatus was developed to study the pyrolysis products of fuels as a function of temperature, residence time, and atmospheric composition. Preliminary data were obtained on the analysis of fuel degradation products.

IV. FUEL CHARACTERIZATION

A. Fuel Physicochemical Properties

Four fuels representative of DF-1, DF-2, high-aromatic content light cycle oil, and JP-8 were characterized for their physicochemical properties. Fuel properties determined by standard laboratory procedures are listed in TABLE 1. These properties include ASTM D 86 distillation range, flash point, heats of combustion, elemental analysis, density, and viscosity. The hydrocarbon-type analyses for aromatic, olefins, and saturates by D 1319 are also included in the table.

B. Fuel Thermophysical Properties

The thermophysical properties, including heat capacity, thermal conductivity, and heats of vaporization, are presented in TABLE 2. The heat capacity and the heat of vaporization were determined by differential scanning calorimetry (DSC). The DSC thermograms are presented in Figs. A-1 through A-3 in the appendix. A DuPont model 990 thermal analyzer with a DSC cell was used to generate the thermograms. In DSC, the sample material is subjected to a linear temperature program, and the heat flow rate into the sample is continuously measured. To establish a baseline, the calorimeter was programmed at $10^{\circ}C/min$ to heat an empty, unsealed sample pan over the 25° to $350^{\circ}C$ temperature range. The program was then repeated for a hermetically sealed sample pan containing a weighed sample of fuel. The specific heat of the sample is calculated from the difference between the two sets of measurements. The hermetically sealed sample container can withstand at least three internal atmospheres (45 psia) prior to rupture. The closed container prevents vaporization of the fuel in the temperature range that produces 45 psia. Thus up to the point of rupture, the endotherm is a true measure of heat capacity; after the rupture, the endotherm is a measure of heat of vaporization. The DSC peaks between the temperatures of 175° and $300^{\circ}C$ in the thermograms are due to the heat of vaporization of the fuel after the rupture of the sample containers. The variation in the heat capacity as a function of temperature was not significant for the fuels examined; therefore, the values at $40^{\circ}C$ are reported in TABLE 2. The heat capacities among the fuels ranged in values from 0.4 to 0.54 $cal/g^{\circ}C$. The heats of vaporization reported in the table were calculated from the areas under the endothermic DSC peaks.

TABLE 1. Properties of Fuels Selected for Flammability Characteristics

Fuel	DF-1	DF-2	JP-8	Lt. Cycle Oil
Distillation, ASTM D 86, °F (°C)				
IBP	378 (192)	370 (188)	302 (150)	370 (188)
10%	430 (221)	417 (214)	359 (182)	473 (245)
50%	461 (238)	496 (258)	426 (219)	530 (277)
90%	484 (251)	598 (314)	493 (256)	619 (326)
EP	539 (282)	650 (343)	543 (284)	653 (345)
Hydrocarbon Type, ASTM D 1319, vol% (by FIA)				
Aromatics	24.44	32.2	17.9	77.9
Olefins	2.26	1.2	1.4	--
Saturates	73.30	66.2	80.7	22.1
Flash Point, °F (°C)	150 (66)	158 (70)	145 (63)	184 (84.4)
Heat of Combustion,				
Gross Btu/lb	19,635	19,477	19,757	18,534
(mg/kg)	(45.67)	(45.30)	(45.96)	(43.109)
Net Btu/lb	18,434	18,295	18,325	17,593
(mg/kg)	(42.88)	(42.556)	(42.62)	(40.92)
Elemental Analysis, wt%				
Carbon	86.71	86.5	86.54	88.78
Hydrogen	13.17	12.95	13.75	10.32
Nitrogen	--	0.012	0.00	0.026
Sulfur	0.01	0.36	0.03	0.42
Specific Gravity at 60°F (15°C)	0.8338	0.8493	0.8185	0.9390
Viscosity, cSt at 40°C	1.86	2.5	1.10	3.27

TABLE 2. Thermal Properties of Fuels

Fluid	Heat Capacity, cal gm^{-1} ^{o}C^{-1} at 40°C	Thermal Conductivity, cal sec^{-1} cm^{-1} ^{o}C^{-1} at 40°C	Heat of Vaporization, cal g^{-1}
DF-1	0.51	22.0 X 10^{-5}	48.5
DF-2	0.54	18.4 X 10^{-5}	61.6
JP-8	0.41	22.6 X 10^{-5}	34.4
Light Cycle Oil	0.38	21.1 X 10^{-5}	56.8

The thermal conductivity measurements reported in TABLE 2 were made by a steady-state hot-wire method (ASTM D 2717). The thermal conductivity cell consisted of a straight platinum resistance thermometer located concentrically in a long small-diameter borosilicate glass tube. The thermal conductivity was determined by measurement of the temperature gradient produced across the liquid sample by a known amount of energy introduced into the cell by electrically heating the platinum element.

The four fuels identified in TABLE 1 were further analyzed to describe them in terms of their major components, i.e., aromatics, saturates, cyclo-paraffins, etc., to develop a scheme for blending representative homologue fuels from pure components for in-depth studies. The initial attempt consisted of analysis of the fuels by proton Nuclear Magnetic Resonance (NMR) spectroscopy as described in Reference 3.

The analysis of JP-8 fuel using the proton NMR analysis gave the following results: 3.3 percent aromatic and 96.7 percent aliphatics. A carbon-13 NMR spectrum of the same sample gave 6.9 percent aromatic and 93.1 percent aliphatic. This disparity was further evaluated by normalizing the T1 relaxation times of aromatic and aliphatic carbons by using a proton gated decoupling program on the JEOL FX90Q NMR instrument along with a relaxation agent, Iron (III) acetylacetonate (Fe(AcAc)$_3$). There was still a large difference in values when all carbon-13 NMR spectra were compared; however, the carbon-13 NMR spectrum did give a clearer indication of aliphatic and aromatic carbons present in the fuel mixture than proton NMR spectrum. In addition, the carbon-13 NMR spectrum can lend itself to further interpretation as described by Netzel.[4] Further investigation of the fuel followed Netzel evaluations in order to obtain a good estimation

of fuel composition, e.g., % straight-chain alkanes, average carbon-chain-length, % branched/cyclo-alkanes, and % aromatic. To obtain the necessary data, proton NMR, carbon-13 NMR, FTIR, gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS) were employed.

1. Proton NMR

Proton NMR spectra were obtained on JEOL FX90Q Fourier Transform NMR Spectrometer with a 5-mm probe insert. A 16-μs pulse width (16 μs = 90°), a pulse sequence delay of 200 ms, a sweep width of 1.808 kHz, 8 K data points, and 4 pulses were used to obtain the spectra. The fuel samples were prepared using equal volumes of fuel and deuterated chloroform ($CDCl_3$). The spectra obtained are shown in Figs. A-4 through A-7 in the appendix.

2. Carbon-13 NMR

The carbon-13 NMR spectra were obtained on the above-mentioned instrument with a 5-mm probe insert and, in this case, nongated decoupled spectra were obtained. The parameters used were a pulse width of 3 μs (9 μs = 90°), a pulse sequence delay of 200 ms, a sweep width of 5 kHz and 8 K data points. Five thousand pulses were taken for each spectrum. The spectra obtained are shown in Figs. A-8 through A-11 in the appendix.

3. Carbon-13 NMR (Gated Decoupling)

The carbon-13 NMR spectra obtained by suppression of Nuclear Overhauser Effect (NOE) used the same instrument and samples, with only the addition of $Fe(AcAc)_3$ to make the solution 0.1M in $Fe(AcAc)_3$. A pulse width of 6 μs (9 μs = 90°), a pulse sequence delay of 5s, a sweep width of 5 kHz, and 8 K data points were used. Gated decoupling was used to suppress the NOE. The spectra obtained under these conditions are shown in Figs. A-12 through A-15 in the appendix.

4.   GC/MS

The GC/MS data were obtained on a Finnigan 3300 using a Tracor 560 GC. The capillary column was a DB-5 fused silica (30 meter X 0.25 mm). The injector, detector, and transfer interface temperatures were 255°, 110°, and 255°C, respectively. The temperature program was initiated at 40°C, and held for 2 minutes. The ramp rate was 10°C per minute to a final temperature of 295°C. The samples were diluted to 10 µg/L, and 1 to 2 µL were injected. The results of the GC chromatograms are shown in Figs. A-16 through A-19 in the appendix.

The FTIR spectra were obtained on a Digilab FTS-15E. The samples were run as films between salt disks at a resolution of 4 cm^{-1}. The spectra were printed as absorbances for the purpose of ratioing the aliphatic and aromatic components as reflected by the absorbance at 2950 and 3055 cm^{-1}. The FTIR spectra are shown in Figs. A-20 through A-23 in the appendix.

V. FORMULATION OF IDEALIZED FUEL BLENDS

The aliphatic/aromatic content and chemical identification of the real fuels were determined using proton and carbon-13 NMR and GC/MS. The aliphatic/aromatic content determined by each method is compared in TABLE 3. For the DF-2 and light cycle fuel, the ratio of aliphatic to aromatic compounds determined by each method of analysis does not vary significantly. However, for JP-8 and DF-1 fuels, the aromatic content measurements are considerably higher by GC/MS than NMR methods. The GC/MS method was thought to be more reliable than the other.

TABLE 3. Comparison of GC/MS with Proton and Carbon-13 NMR Analysis

Fuel	Proton NMR		Carbon-13 NMR*		GC/MS	
	Percent Aliphatic	Percent Aromatic	Percent Aliphatic	Percent Aromatic	Percent Aliphatic	Percent Aromatic
JP-8	96.7	3.3	91.1	8.9	76.8	23.3
DF-2	89.8	10.2	86.6	13.4	89.1	10.9
Light Cycle Oil	52.7	47.3	48.3	51.7	57.1	42.9
DF-1	94.0	6.0	84.4	15.6	74.0	26.0

* Carbon-13 NMR run using no NOE.

The GC/MS method utilized collection of the total ion current for the entire chromatographic run and produced reconstructed ion chromatograms. The aliphatic and aromatic components of the fuel mixture were differentiated by reconstructed ion chromatograms. The area counts for aromatics of substituted benzene, naphthalenes, and other polynuclear aromatics were combined. Similarly the area counts for aliphatics, both linear and branched, were combined. This method not only determines the percent aliphatic and aromatic character of the fuel but also enables characterization of the fuel components by mass spectral fragmentation patterns and molecular ions.

Fig. 1 shows the GC chromatogram of the DF-2 fuel. The assignments of the identity of the peaks was done by MS as shown, for example, in Fig. 2.

A synthetic blend representative of the DF-2 based on the GC/MS analysis should contain at least one component from each of the areas A, B, and C as shown in Fig. 1. The suggested components are normal alkanes $C_{10}H_{22}$, $C_{16}H_{34}$, and $C_{22}H_{46}$. Also, the type of aromatic components observed are C1, C2, and C3 substituted benzenes and C1 and C2 substituted naphthalenes. Therefore, the representative aromatic components should be C2 substituted benzenes and C2 naphthalenes. Thus, the final blend composition of the idealized fuel would contain the following:

Component	Percentage
$n\text{-}C_{10}H_{22}$	19%
$n\text{-}C_{16}H_{34}$	57%
$n\text{-}C_{22}H_{46}$	14%
C2-benzenes	5%
C2-naphthalenes	5%

Similar analysis of the other fuels afforded the composition of idealized fuel blends from pure hydrocarbons is listed in TABLE 4.
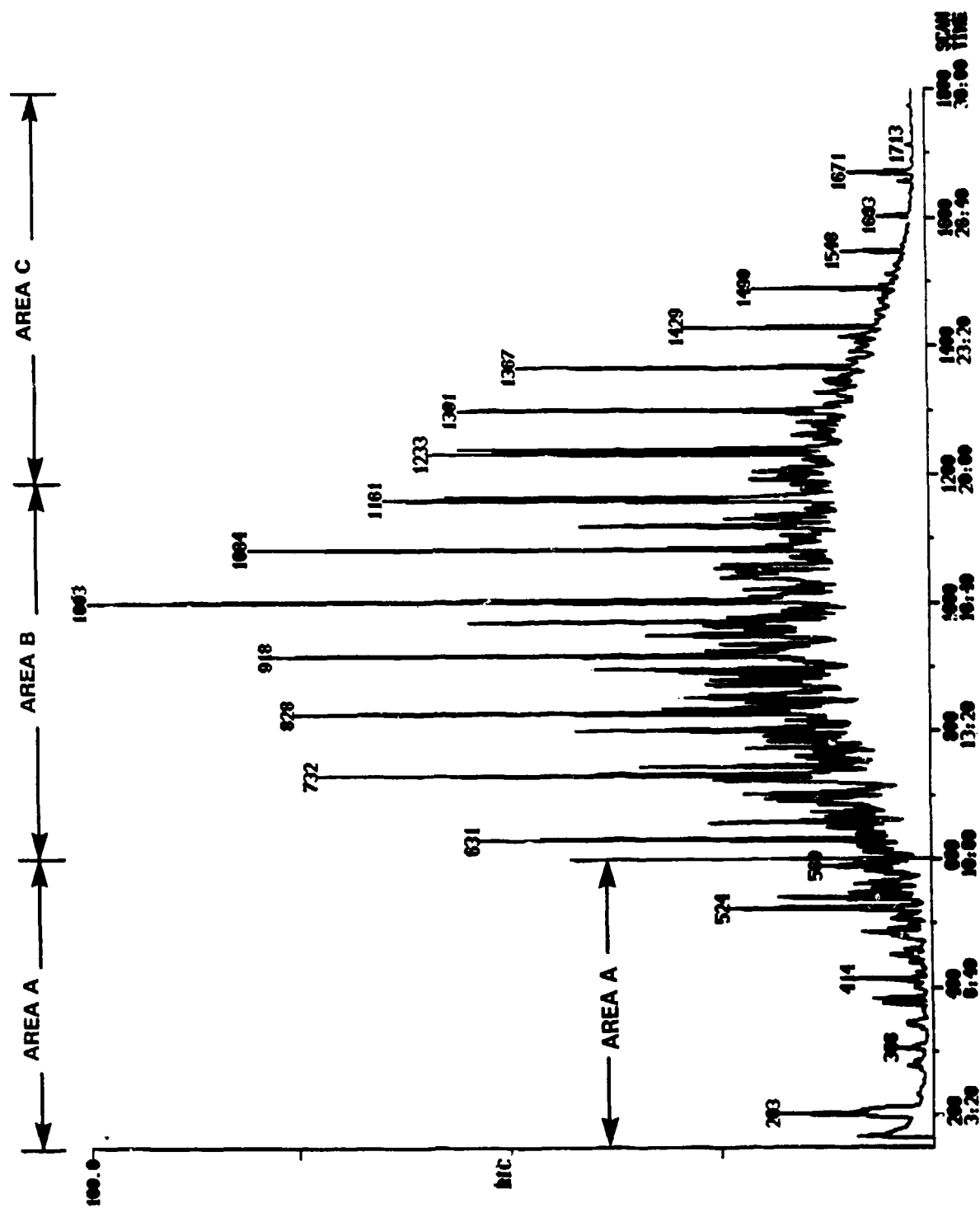
Figure 1. Gas chromatography chromatogram of fuel DF-2 with representative areas of component selection for normal alkanes

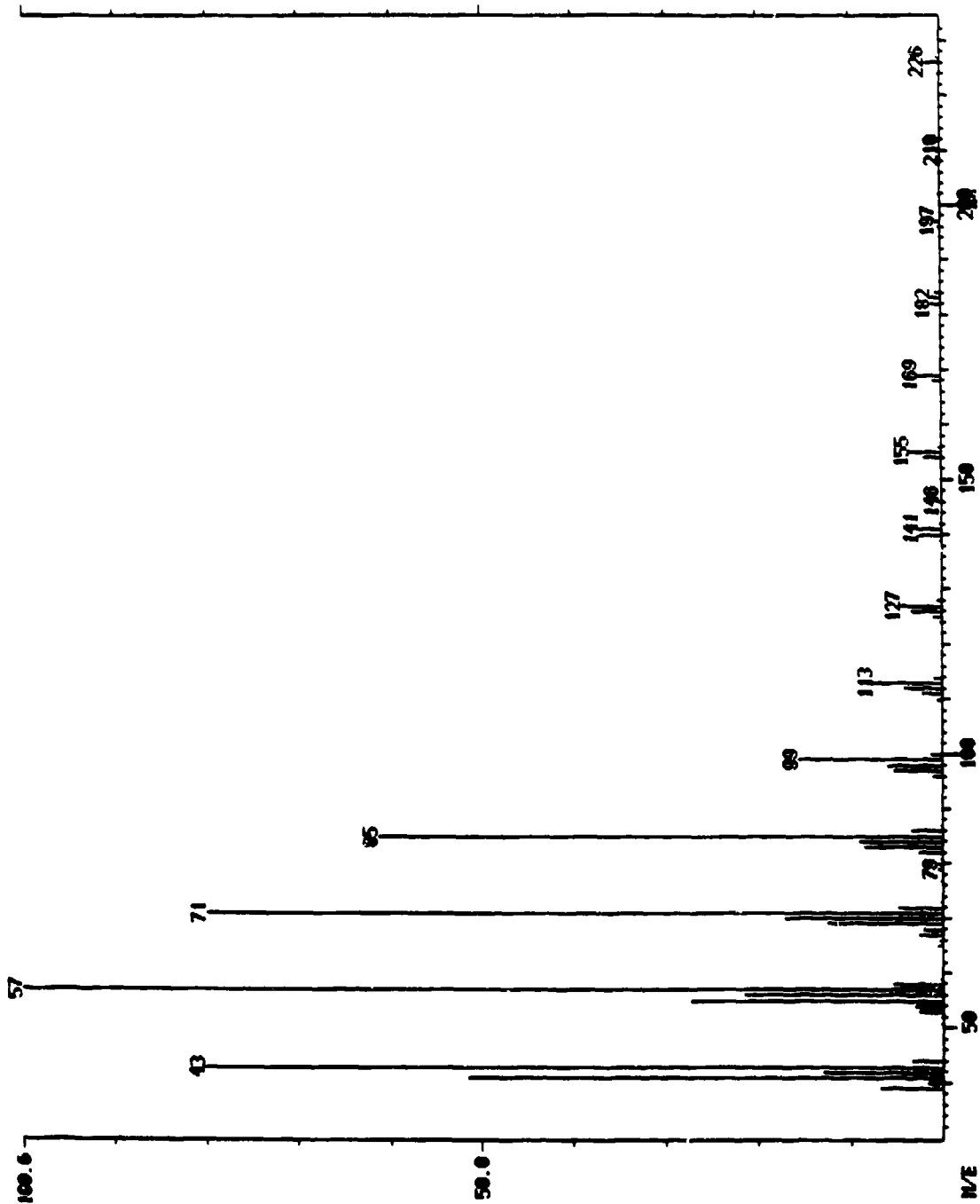(The aromatic components are the smaller peaks in the noisy baseline)

Figure 2. The mass spectrum of scan No. 1084 in Fig. 1 corresponding to n–$C_{16}H_{34}$ alkane
(The fragmentation pattern suggests it is linear)

TABLE 4. Idealized Fuel Blends

Fuel	% Aliphatic/ % Aromatic	Component	Wt%
DF-1	74/26	$C_{10}H_{22}$	24
		$C_{13}H_{28}$	50
		o-xylene	26
Light Cycle Oil	57/43	$C_{16}H_{34}$	28
		$C_{18}H_{38}$	29
		1-Methylnaphthalene	36
		1,2,3-Trimethylbenzene	07
JP-8	77/23	$C_{10}H_{22}$	08
		$C_{13}H_{28}$	69
		Dimethyl Naphthalene Mixture	15
		1,2,3-Trimethylbenzene	08
DF-2	90/10	$C_{10}H_{22}$	19
		$C_{16}H_{34}$	57
		$C_{22}H_{46}$	14
		C_2-Benzenes	05
		C_2-Naphthalenes	05

VI. THERMAL DECOMPOSITION OF FUELS

This phase of the investigation determined the vapor phase composition of the fuels as a function of its pyrolysis temperature and environment. The preliminary work was carried out by using pyroprobe/GC/MS at various temperatures in helium and air. The vapor compositions of fuels did not significantly change from their liquid compositions using the pyroprobe at temperatures ranging from 350° to 1000°C in inert atmospheres. This absence of thermal degradation was due to extremely short residence times of the fuels at the pyrolysis temperatures in the analytical pyroprobe. Therefore, a high-temperature flow reactor was developed to conduct thermal degradation experiments in carefully controlled conditions of temperatures and flows, allowing longer residence times.

A. Pyrolysis/GC/MS

A CDS - Model 120 Pyroprobe was used in conjunction with GC/MS as shown in Fig. 3. In these experiments, a thin layer of fuel was coated on the heating ribbon of the pyroprobe. The probe was located in the pyrolysis oven swept by the carrier gas
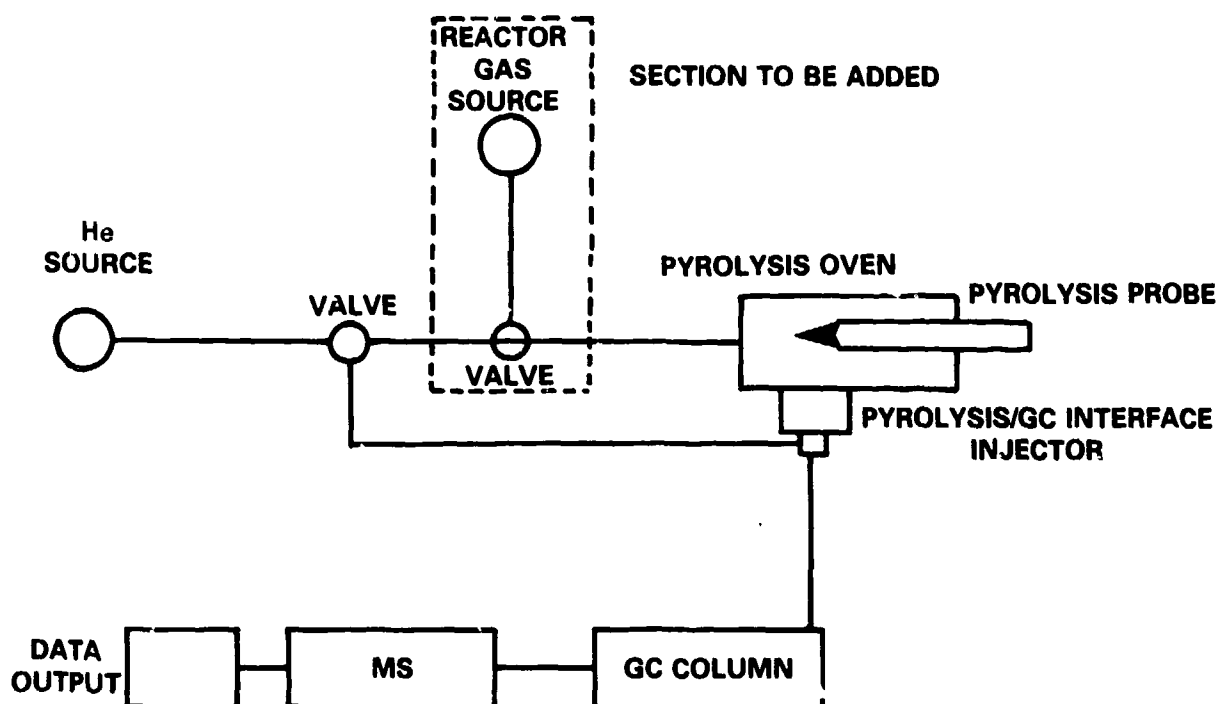
Figure 3. Block diagram of pyrolysis system

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(helium). The pyroprobe ribbon was brought up to the set temperatures ⎯f 350°, 700°, or 1000°C within 0.1 second, and then maintained at that temperature for 10 seconds.

The chromatograms of each real fuel at each temperature are presented in Figs. A-24 through A-35 in the appendix. Examination of the figures revealed no significant difference in the vaporized material for any fuel at the three different temperatures; that is, the volatilized material was essentially constant in the composition for a given fuel, indicating distillation of the fuel in inert carrier gas. The thin film of the fuel did not stay in contact with the pyroprobe throughout the full temperature range, but rather vaporized in its distillation temperature range. The vapors were carried off in helium. This was further verified by blending fuels of known composition and conducting the same study as above. The largest difference, if any, would be seen between temperatures of 1000°C versus 350°C.

These two pyrolysis temperatures were used on the synthetic blends shown in TABLE 4. The GC chromatograms are shown in Figs. A-36 through A-43. Again there was no apparent variation of the components present as volatiles at 350°C versus 1000°C. The ratios of components were different but not to the degree expected. Thus, the pyroprobe analysis of real fuels and idealized fuel blends under inert atmosphere yielded apparent boil-off of the fuel components.

B.   Flow Reactor

Further thermal degradation studies were continued using a high-temperature flow reactor apparatus as shown in Fig. 4. This apparatus consists of a reaction chamber 1-in. OD X 5.5-in. long X 1/8-in. thick (2.5 cm X 14 cm X 0.3 cm) wall stainless steel cylinder with capped ends. The reactor tube was enclosed in a 6-in. (15 cm) long X 1 1/4-in. (3.2 cm) diameter muffle furnace. The operating temperature limit of the furnace is 1000°C. The cylindrical chamber has sealed ends and penetrations for gas/liquid inlets, outlets, and various thermocouples.

The liquid flow was controlled by a precision metering syringe pump, and the gas flow was metered by a rotameter. The reaction products were carried to a condensor/separator tube at 30°C.
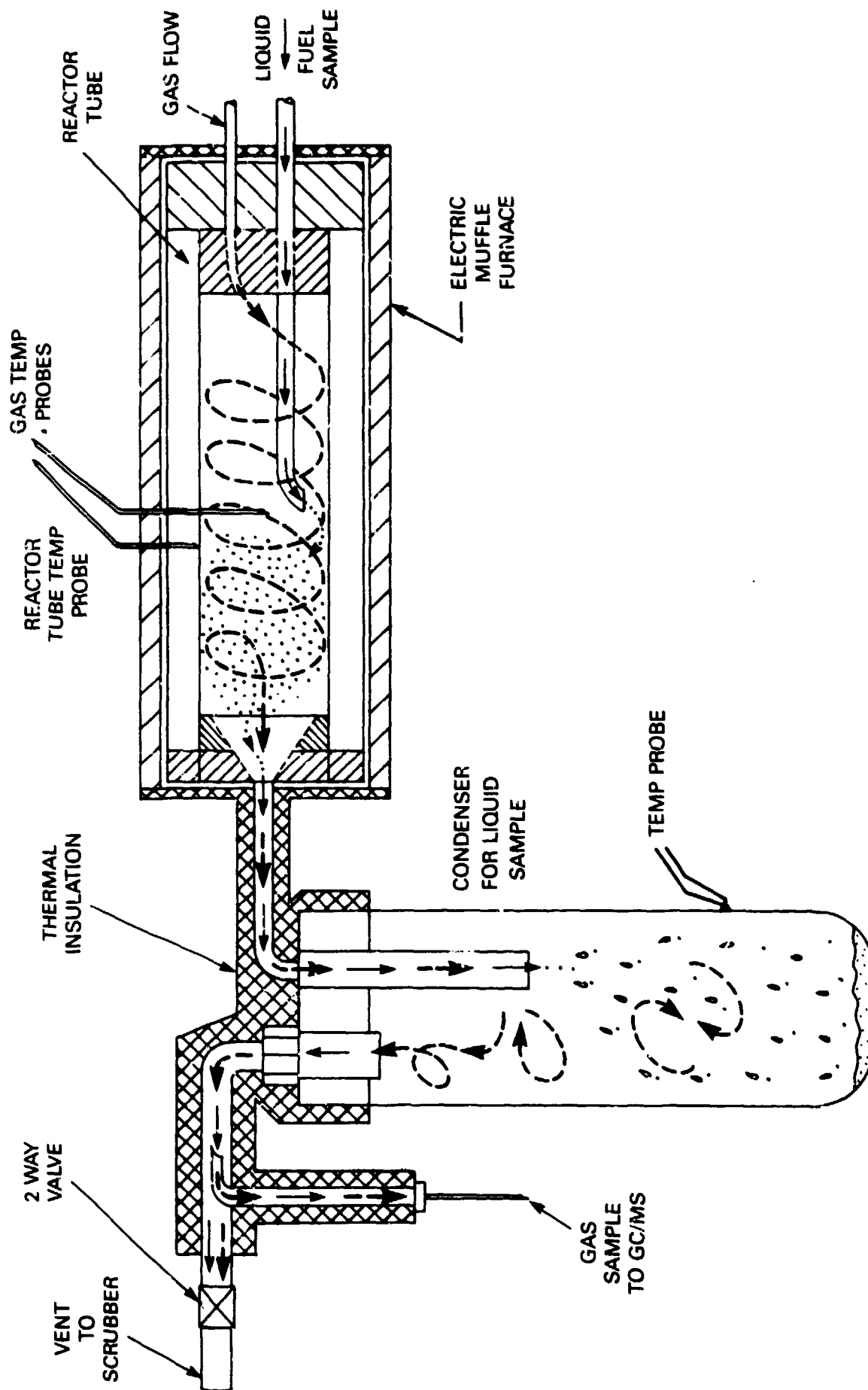
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Figure 4. High-temperature flow reactor for thermal degradation of fuels

GAS FLOW

LIQUID FUEL SAMPLE

REACTOR TUBE

ELECTRIC MUFFLE FURNACE

GAS TEMP PROBES

REACTOR TUBE TEMP PROBE

THERMAL INSULATION

CONDENSER FOR LIQUID SAMPLE

TEMP PROBE

2 WAY VALVE

GAS SAMPLE TO GC/MS

VENT TO SCRUBBER

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The apparatus was operated under steady-state at 600°C wall temperature and helium flow rate of 200 mL/min and fuel flow rate of 1.55 mL/min. The gas and condensate exhausts were analyzed by GC/MS.

A long chain alkane n-$C_{16}H_{34}$ was used as a test liquid to determine the above minimum temperature and flow conditions that produced significant thermal cracking products. These products in both the gas exhaust and condensate collections are listed in TABLE 5. The conditions for the gas chromatograph/mass spectrometers are listed in TABLE 6. The products observed were mostly alkenes. These could result from pyrolytic cleavage followed by dehydrogenation.

The idealized fuel blends containing pure hydrocarbons were studied next under the conditions employed for the $C_{16}H_{34}$ experiment. The qualitative results for each fuel are presented in TABLE 7 for exhaust gas analysis and TABLE 8 for the exhaust condensate analysis. A number of the thermal cracking products are quite easily seen in the exhaust gas analysis; however, they are present in trace amounts in the condensate. This should be the case since the condensate is continuously swept with the carrier gas. The one significant difference is the gas analysis of JP-8 fuel blend for the condensate analysis in which one was run with an inert carrier and the other was run with added oxygen.

TABLE 5. Pyrolysis Products From $C_{16}H_{34}$ at 600°C for
Both Gas and Condensate Exhaust Systems

Gas	Condensate
1-propene	1-decene
2-butene	1-undecene
2-methylpropane	5-dodecene
1,3-butadiene	3-octadecene
cyclopentane	9-octadecene
1-hexene	1-pentadecene
1-heptene	
2,2,3,3-tetramethylbutane	
1-octene	

TABLE 6. Gas Chromatography/Mass Spectrometry Conditions

Exhaust Gas Analysis

Finnigan 3300 MS

Mass Range:	38-300
Scan Time:	2 sec/scan
Column:	1% SP1000 on Carbopack B 60/80 mesh
	2 m X 2 mm ID
Program:	100°C||15°C per minute||230°C
Electron Impact	

Exhaust Condensate Analysis

Finnigan 4600 MAT

Mass Range:	38-525
Scan Time:	1 sec/scan
Column:	DB-5, 0.25 mm ID/0.25 micron film thickness
	30 meters
Program:	50°C||10°C per minute||295°C
Carrier Gas:	He, 1 mL/min
Inj. Temp.:	275°C
Interface Temp:	275°C
Electron Impact	

TABLE 7. Exhaust Gas Analysis of Idealized Fuel Blends

Fuel	Original Components	Exhaust Gas Components
JP-8	$C_{10}H_{22}$, 8% $C_{13}H_{28}$, 69% dimethylnaphthalene mixture, 15% 1,2,3-trimethylbenzene, 8%	1-propene 2-butene cyclopentane 1-hexene 1-heptene
DF-1	$C_{10}H_{22}$, 24% $C_{13}H_{28}$, 50% o-xylene, 26%	1-propene 2-butene cyclopentane 1-hexane 1-heptene
DF-2	$C_{10}H_{22}$, 19% $C_{16}H_{34}$, 57% $C_{22}H_{46}$, 14% C-2 benzene, 5% C-2 naphthalenes, 5%	1-propene 2-butene 1-pentene 1-hexene
Light Cycle Oil	$C_{16}H_{34}$, 28% $C_{18}H_{38}$, 29% 1-methylnaphthalene, 36% 1,2,3-trimethylbenzene, 7%	1-propene 2-butene cyclopentane 1-hexene 1-heptene 1,2-dimethylbenzene
JP-8 (w/6% O_2/N_2 as carrier gas)	$C_{10}H_{22}$, 8% $C_{13}H_{28}$, 69% dimethylnaphthalene mixture, 15% 1,2,3-trimethylbenzene, 8%	1-propene 2-butene cyclopentane 1-hexene 1,2-dimethylcyclopentane 1-heptene

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TABLE 8. Exhaust Condensate Analysis of Idealized Fuel Blends

Fuel	Original Composition	Exhaust Condensate Components
JP-8	$C_{10}H_{22}$, 8% $C_{13}H_{28}$, 69% dimethylnaphthalene mixture, 15% 1,2,3-trimethylbenzene, 8%	1-octene 1-nonene decane 1,2,3-trimethylbenzene 1-ethenyl-2-methylbenzene 1-undecene 1-dodecene tridecane dimethylnaphthalous 4-methyl-1,1'-biphenyl hexadecane
DF-1	$C_{10}H_{22}$, 24% $C_{13}H_{28}$, 50% o-xylene, 26%	1-octene 1-nonene o-xylene decane trimethylbenzene 1-ethenyl-2-methylbenzene undecene dodecene tridecene tridecane methylnaphthalene dimethylnaphthalene acenaphthene undecene hexadecane
DF-2	$C_{10}H_{22}$, 19% $C_{16}H_{34}$, 57% $C_{22}H_{46}$, 14% C-2 benzene, 5% C-2 naphthalenes, 5%	1-octene o-xylene decane undecane hexadecane $C_{22}H_{46}$
Light Cycle Oil	$C_{16}H_{34}$, 28% $C_{18}H_{38}$, 29% 1-methylnaphthalene, 36% 1,2,3-trimethylbenzene, 7%	1-octene 1-nonene 1,2,3-trimethylbenzene 1-methylnaphthalene hexadecane octadecane
JP-8 (w/6% O_2/N_2 as carrier gas)	$C_{10}H_{22}$, 8% $C_{13}H_{28}$, 69% dimethylnaphthalene mixture, 15% 1,2,3-trimethylbenzene, 8%	1-octene 1,2,3-trimethylbenzene methylnaphthalene 1-ethenyl-2-methylbenzene

VII. BALLISTIC PENETRATION SIMULATON

Some preliminary experiments were conducted during this project to address and simulate the events within the fuel cell just after the first wall penetration. The primary thermal source under these conditions is the jet of high-temperature aluminum metal due to rapid localized deformation fracture of the aluminum armor. A few exploratory and fully instrumented experiments were conducted with a plasma arc transfer cutting torch as an energy source (Fig. 5). The target was an 18-in. aluminum plate in contact with liquid at its lower surface. The instrumentation consisted of thermocouples to measure skin temperatures and gas/liquid temperatures in the path of penetrating metal particles; radiometers, and total heat flux calorimeters to measure thermal signature of the jet. Documentation consisted of 16-mm motion film coverage. The preliminary experiments showed that the electric noise from the plasma torch itself interfered excessively with the measurement signal. A two-channel isolated instrumentation amplifier was assembled. However, due to lack of funding, testing for its adequacy was not accomplished.

VIII. DISCUSSION AND RECOMMENDATIONS

Pyrolysis experiments conducted in a continuous flow reaction chamber at 600°C with helium as the carrier gas and various fuel blends showed that all fuels produced low molecular weight hydrocarbons in the gas phase due to thermal degradation. The predominant compounds identified were 1-propene and 2-butene along with 1-pentene and 1-hexene in some cases. The fuel blends contained C_{10}, C_{13}, C_{16}, C_{18}, and C_{22} alkanes. These high molecular weight compounds have the lower flammability limit in air from 0.7 to 0.4 vol%; however, their upper limit is approximately 5 vol%. The pyrolysis products of these compounds yielded low molecular weight compounds such as 1-propene and 1-butene. The lower flammability limit of these compounds (2.5 to 1.5 vol%) is higher than the initial compounds; however, their upper limits are in the 10 to 20 vol% range. Thus, in a pyrolysis mixture containing the original compounds as well as the products of thermal degradation, the effective flammable mixture range is 0.4 vol% at lower end to 20 vol% upper limit, as compared to 0.4 to 5 vol% for the original compounds. It is felt that, if these cursory data are correct, this broadening of the flammability limits may help explain why the fuel temperature/flashpoint may not play primary roles of importance. Future tests are recommended with varying reaction
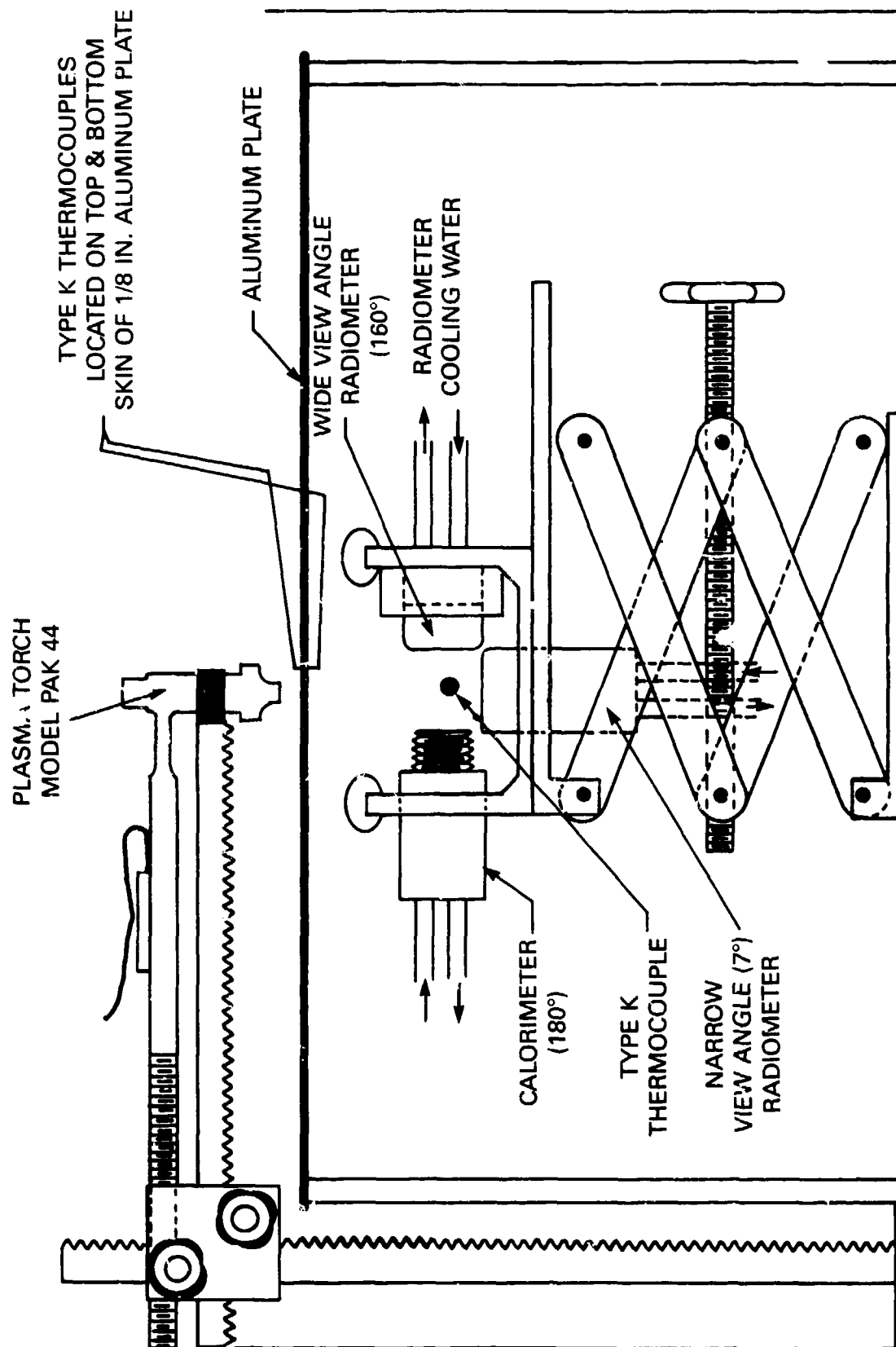
TYPE K THERMOCOUPLES
LOCATED ON TOP & BOTTOM
SKIN OF 1/8 IN. ALUMINUM PLATE

ALUMINUM PLATE

WIDE VIEW ANGLE
RADIOMETER
(160°)

RADIOMETER
COOLING WATER

PLASMA TORCH
MODEL PAK 44

CALORIMETER
(180°)

TYPE K
THERMOCOUPLE

NARROW
VIEW ANGLE (7°)
RADIOMETER

Figure 5. Plasma arc transfer cutting torch as energy source

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temperature, oxygen content in the atmosphere, and quantitative analysis of the exhaust gas/liquid composition in order to develop a higher level of confidence in the data. Additionally, testing should continue on the simulated ballistic penetration experiments in order to better define the parameters associated with ballistic penetration/flame propagation.

V. LIST OF REFERENCES

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2. Kanakia, M.D. and Wright, B.R., "Investigation of Diesel Fuel Fire Vulnerability Parameters in Armored Personnel Carriers," prepared for U.S. Army Belvoir Research and Development Center, Interim Report AFLRL No. 194, AD A155469, DAAK70-85-C-0007, Fort Belvoir, VA, March 1985.

3. Glavincevski, B., Gulder, O.L., and Gardner, L., "Cetane Number Estimation of Diesel Fuels From Carbon Type Structural Composition," SAE Technical Paper Series, No. 841341, presented at the Fuels and Lubricants Meeting and Exposition, Baltimore, MD, 8-11 October 1984.

4. Netzel, D.A., McKay, D.R., Heppner, R.A., Guffey, F.D., Cooke, S.D., Varie, D.L., and Linn, D.E., "Hydrocarbon Type Analysis of Jet Fuels by ^1H and ^{13}C NMR" Fuel, 60, pp. 307-320 (1981).

APPENDIX

DSC AND CHROMATOGRAPHIC DATA
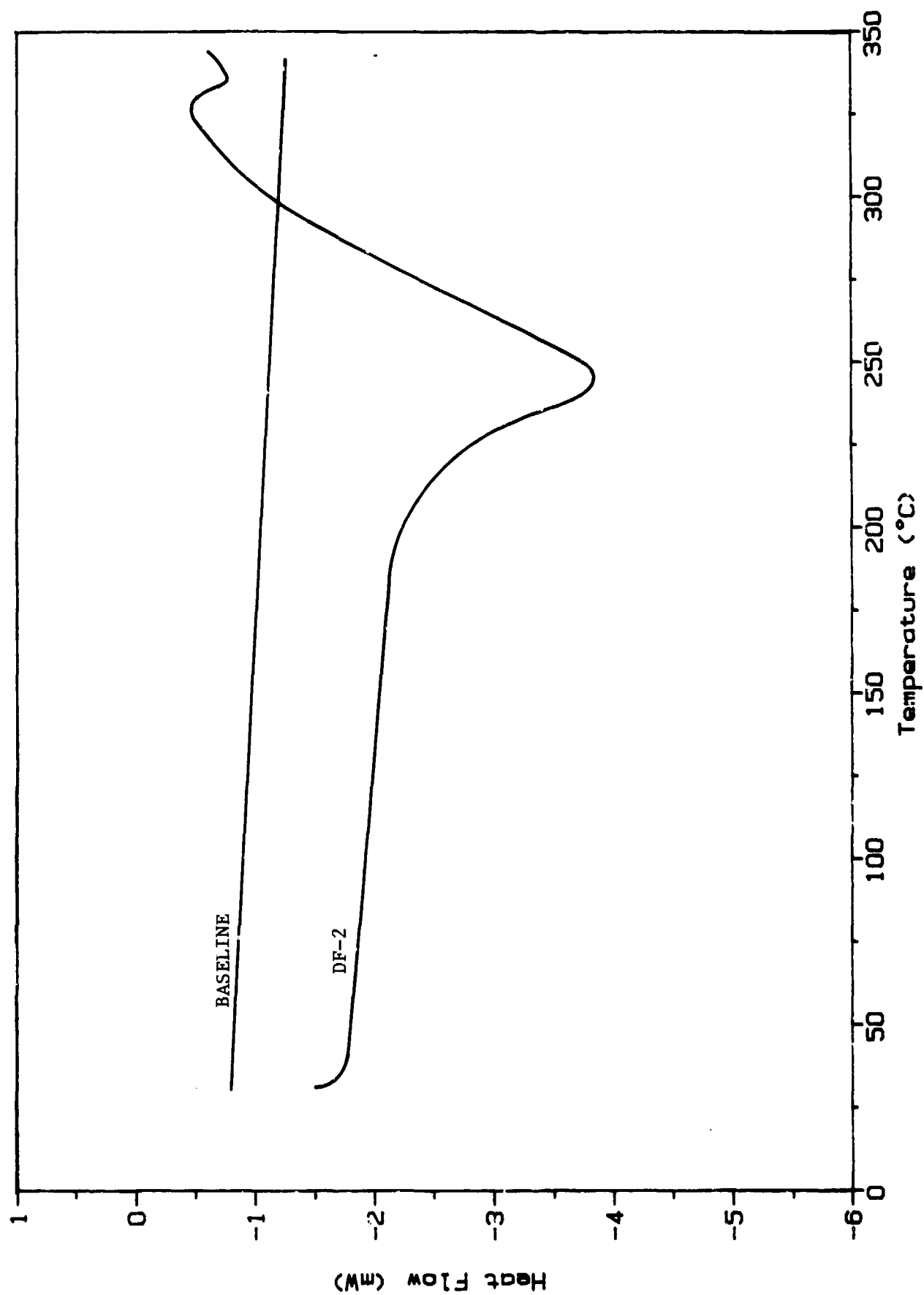
Figure A-1. DSC thermogram of DF-1

25
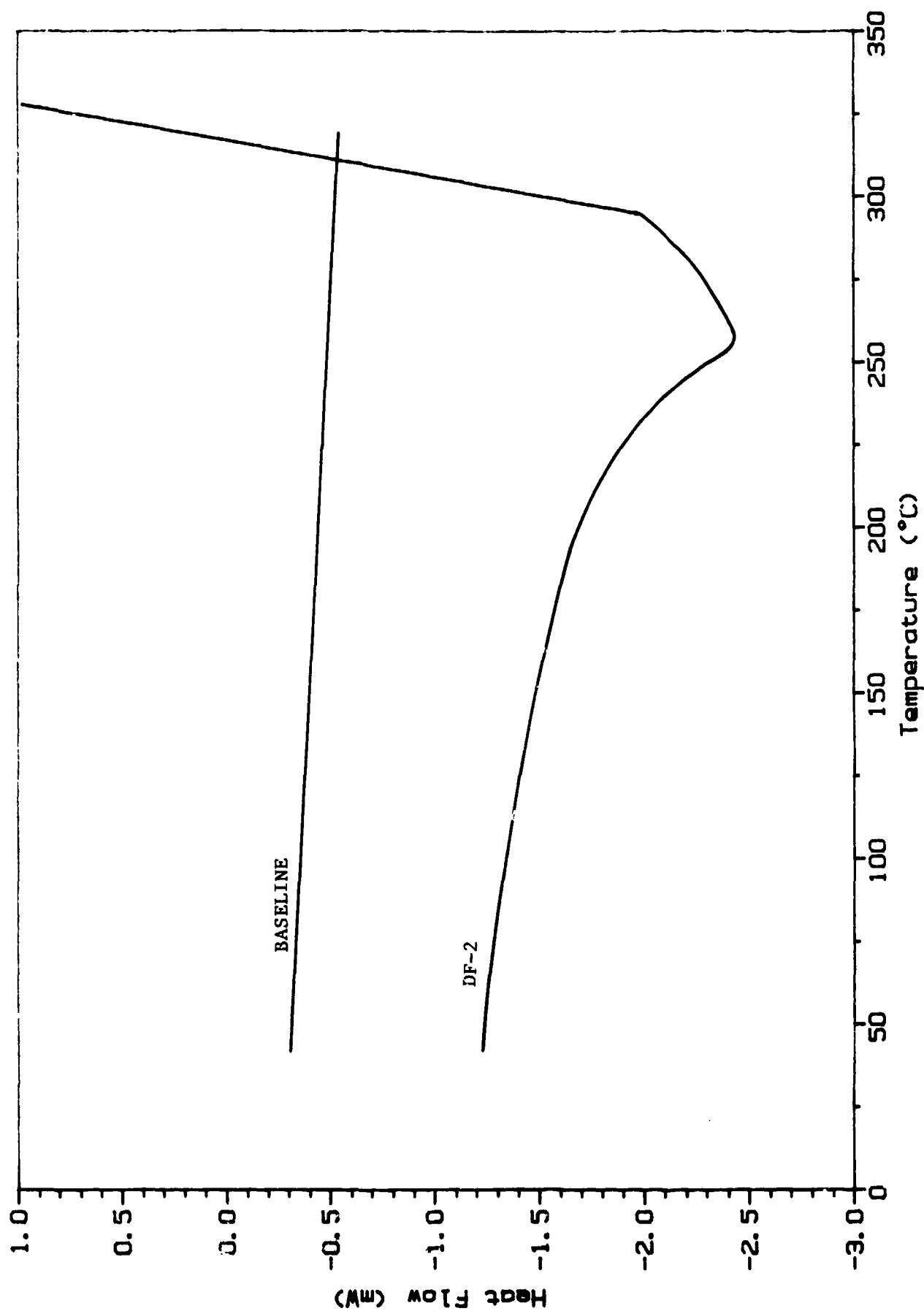
Figure A-2. DSC thermogram of DF-2

26
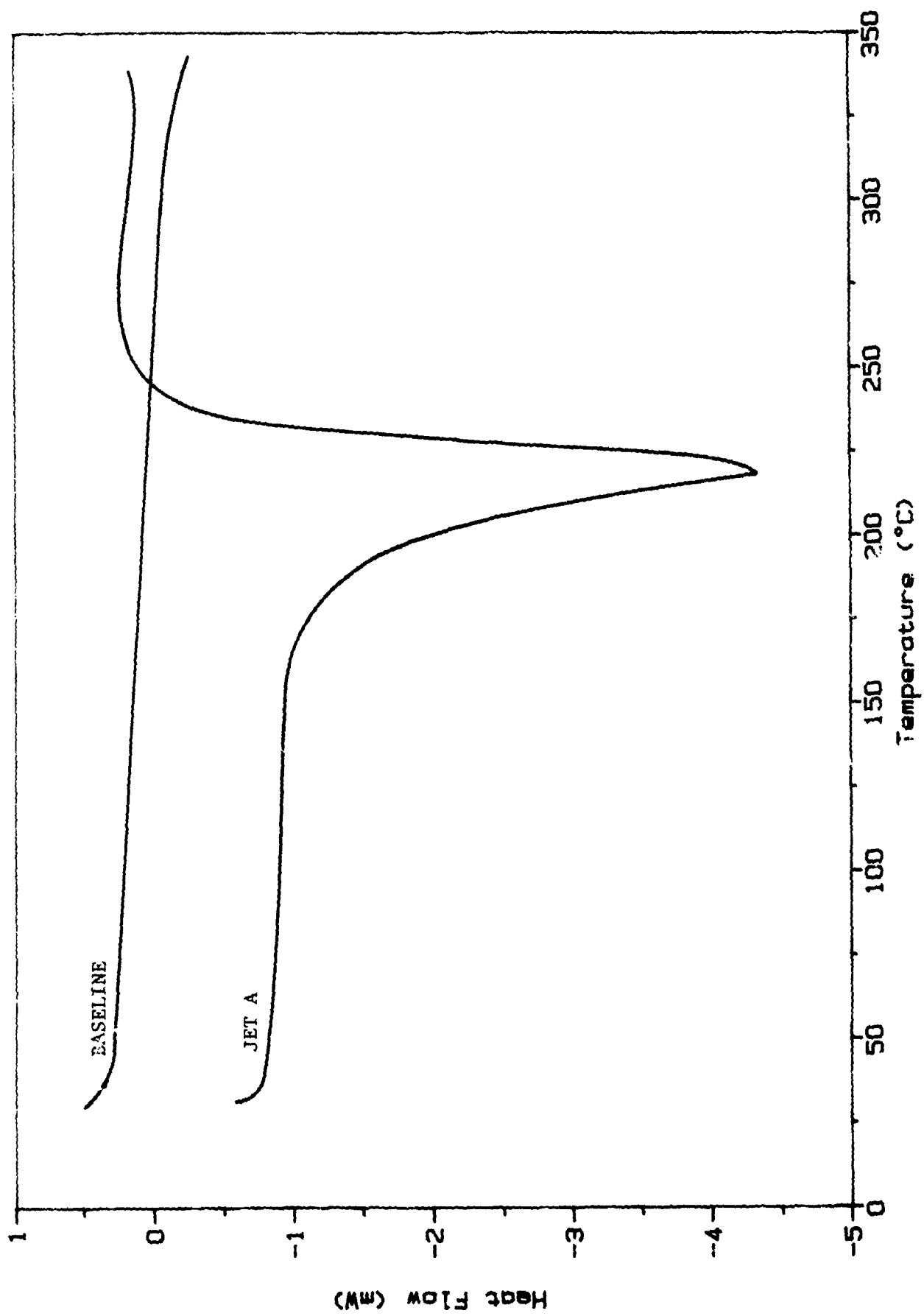
Figure A-3. DSC thermogram of JP-8
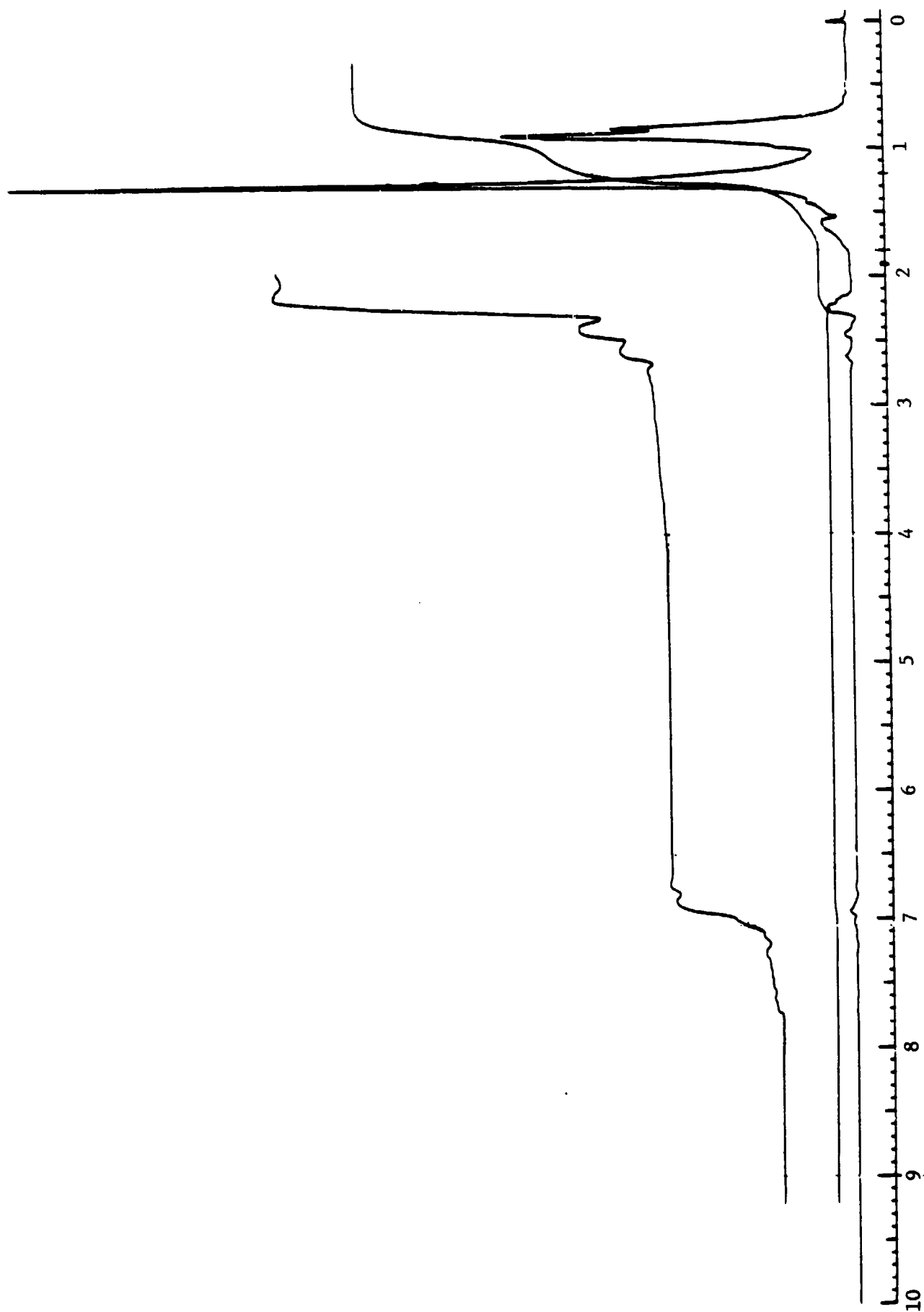
Figure A-4. ¹H NMR spectrum of JP-8

28
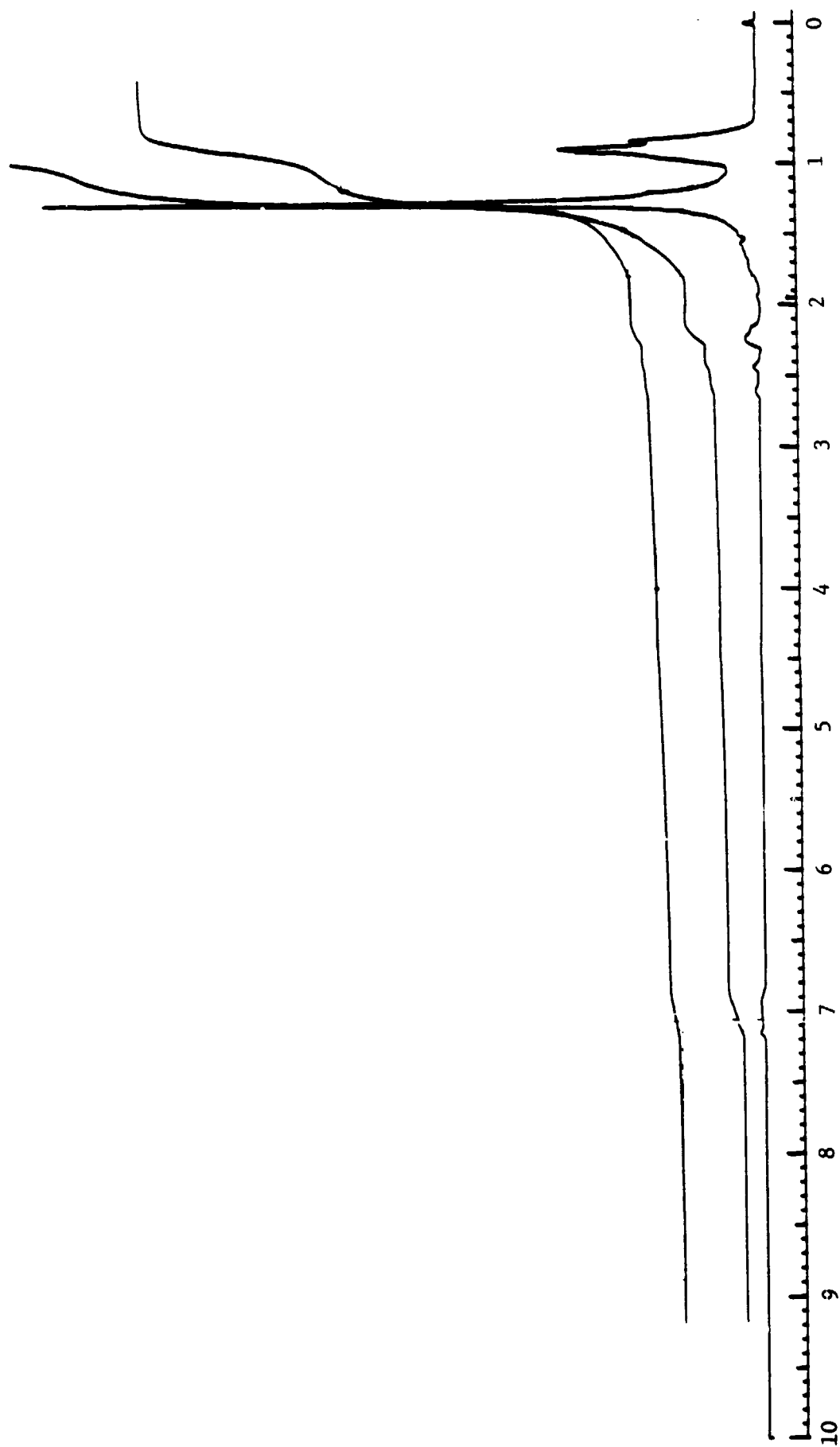
Figure A-5. ^{1}H NMR spectrum of DF-2

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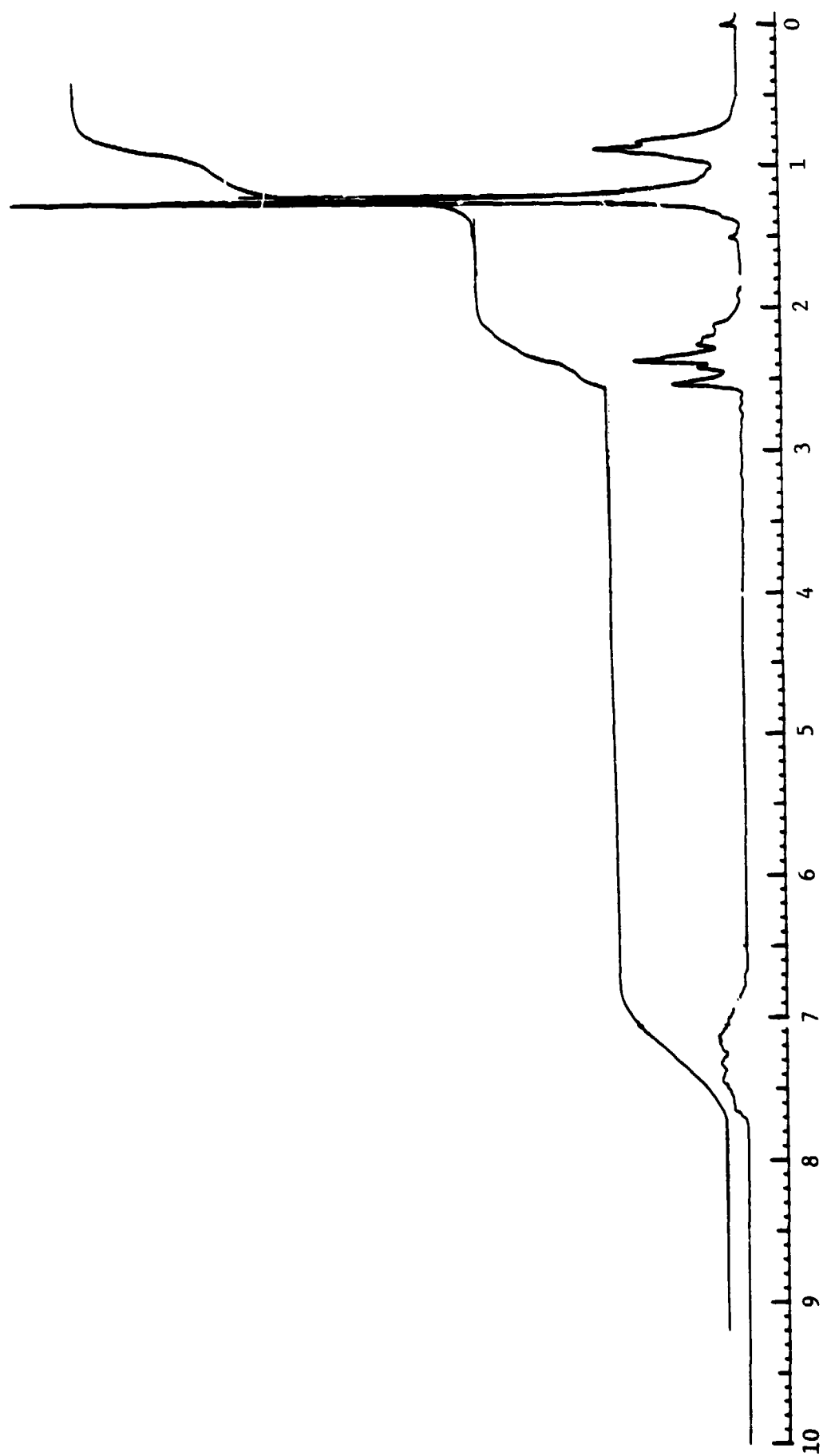
Figure A-6. ^{1}H NMR spectrum of light cycle oil
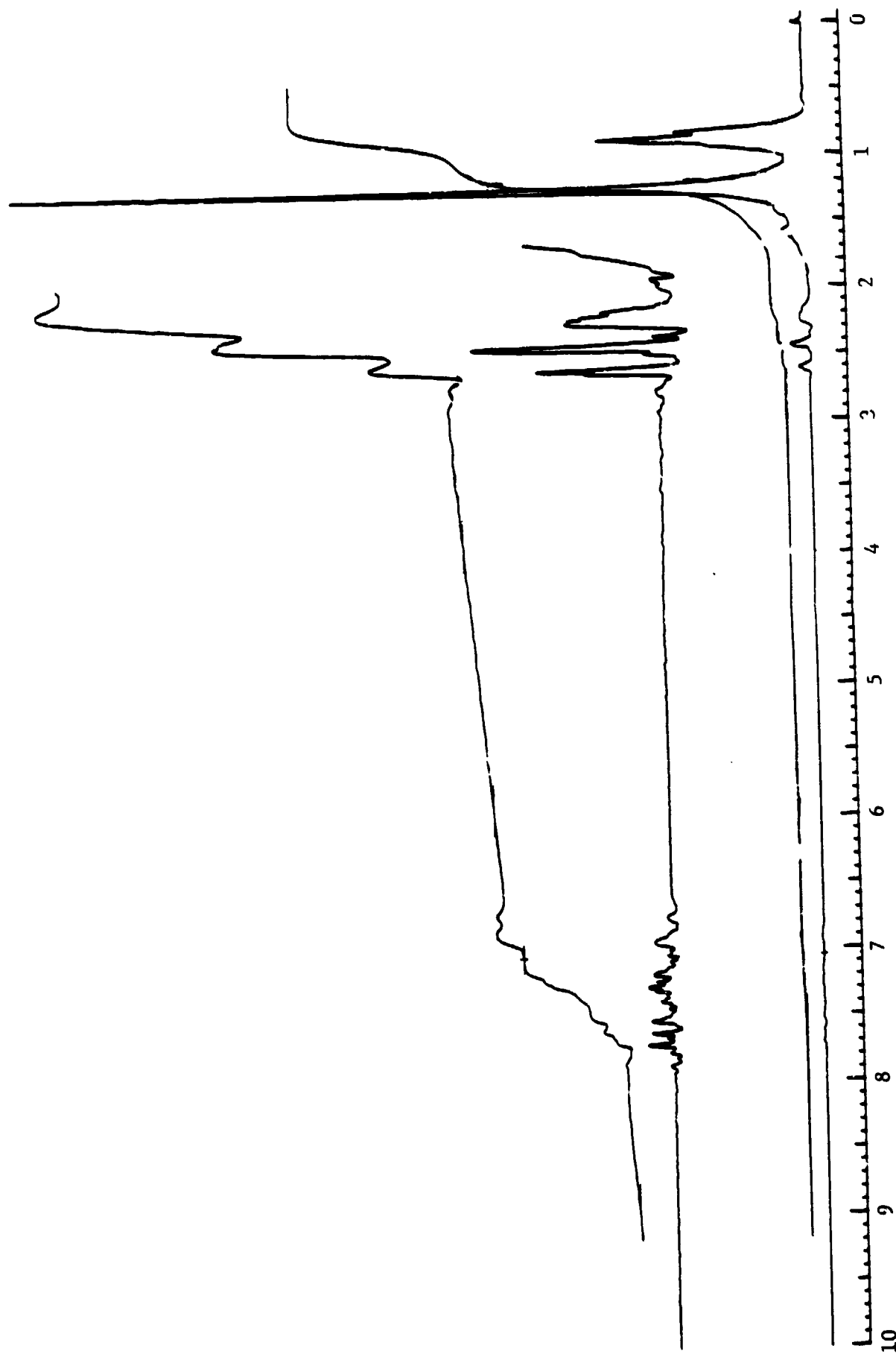
Figure A-7. ^{1}H NMR spectrum of DF-1

31
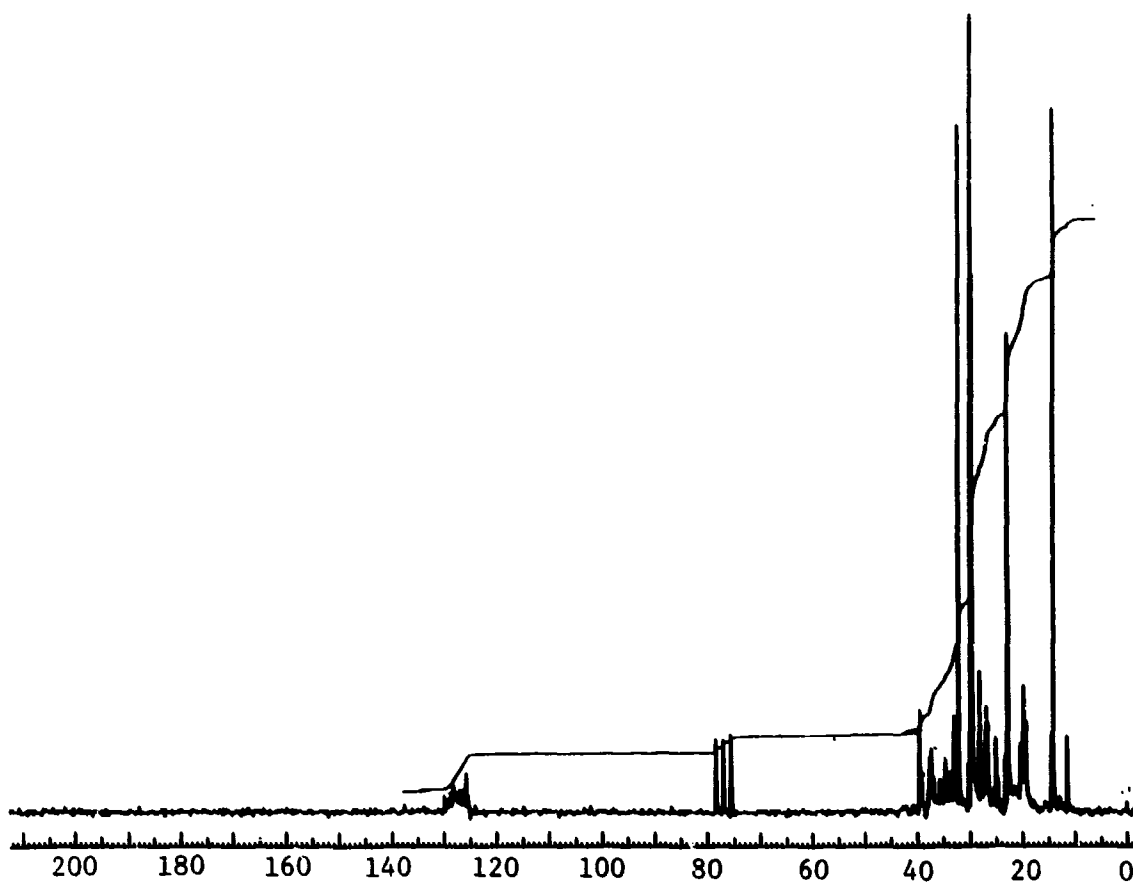
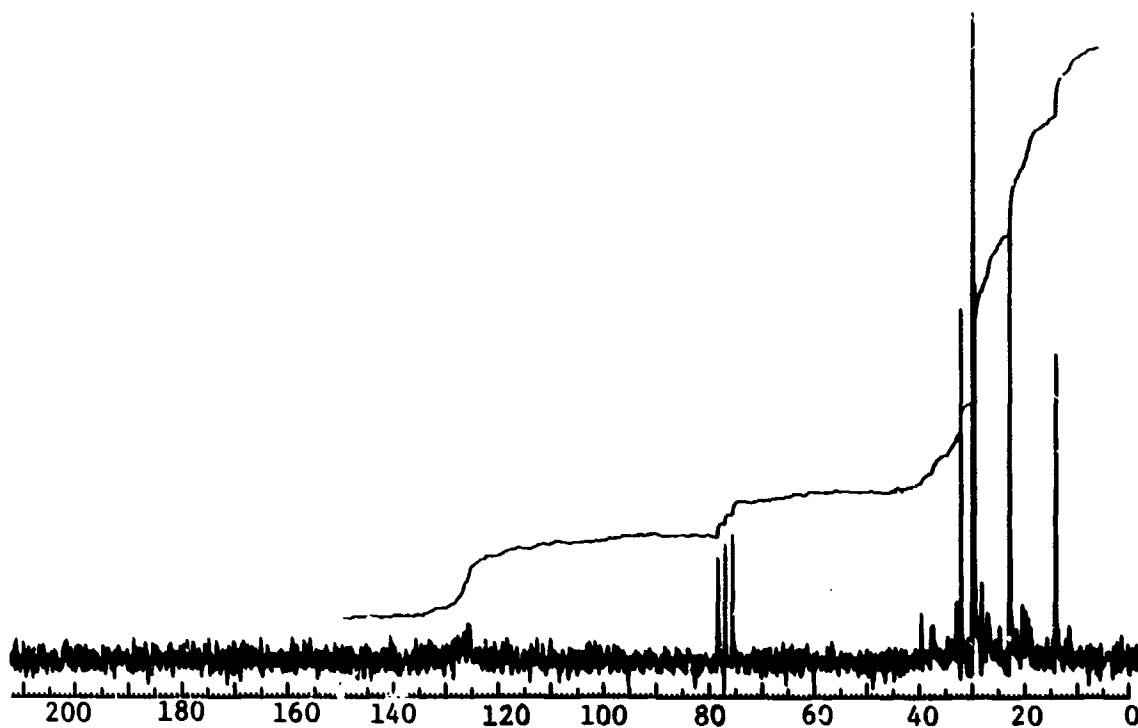Figure A-8. ^{13}C NMR spectrum of JP-8 without NOE suppression
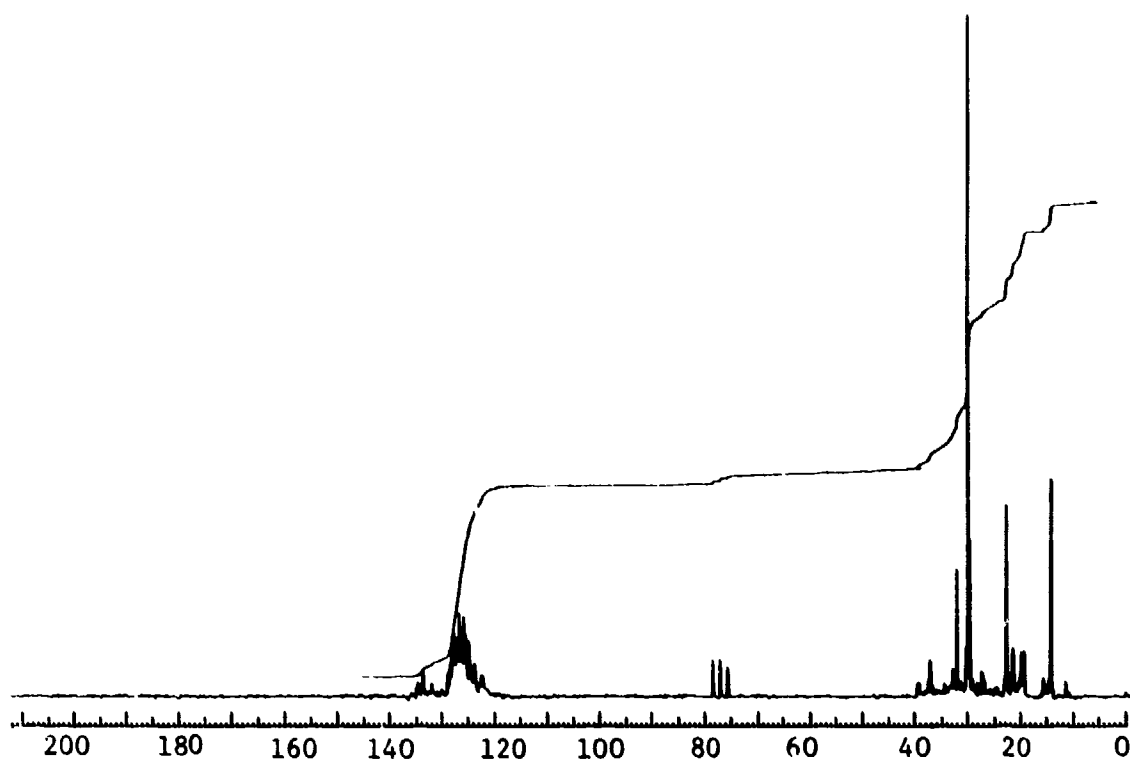

Figure A-9. ^{13}C NMR spectrum of DF-2 without NOE suppression

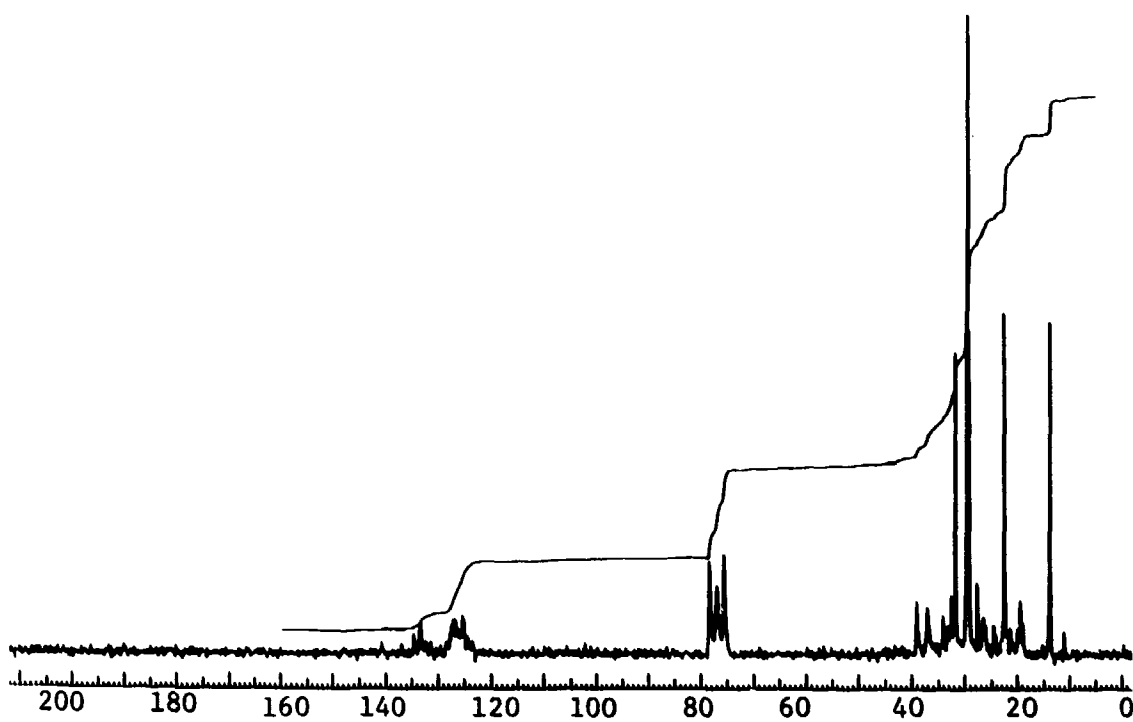Figure A-10. ^{13}C NMR spectrum of light cycle oil without NOE suppression
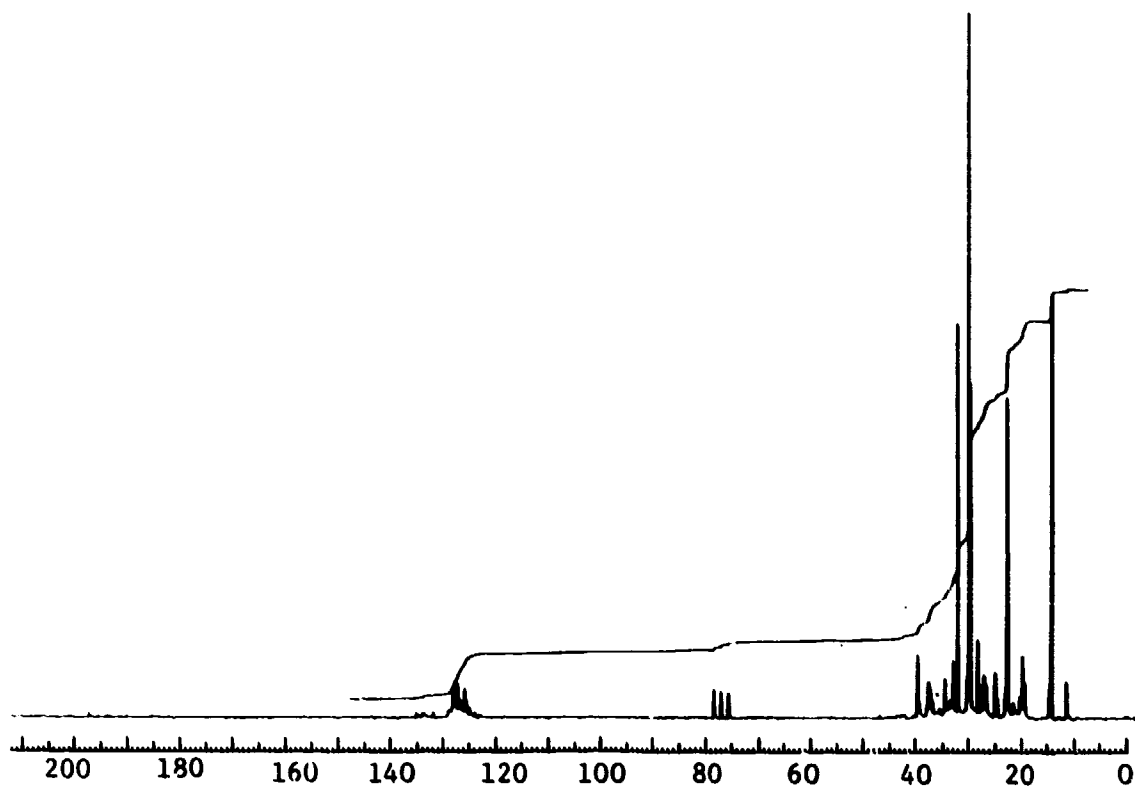
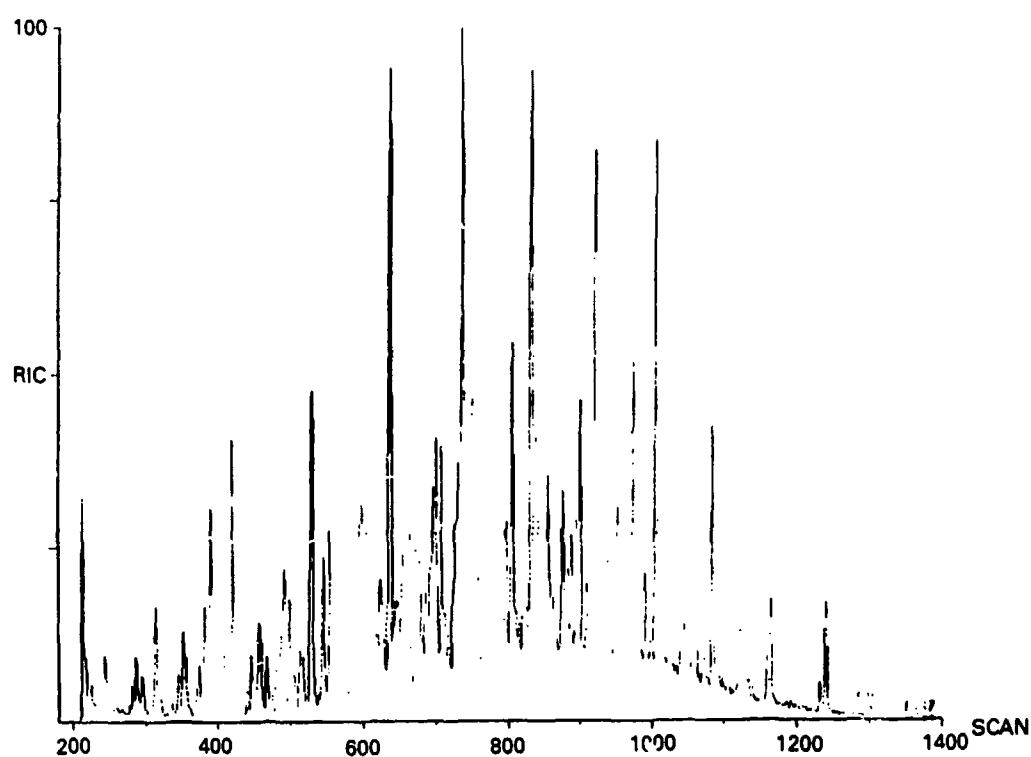Figure A-11. ^{13}C NMR spectrum of DF-1 without NOE suppression

33
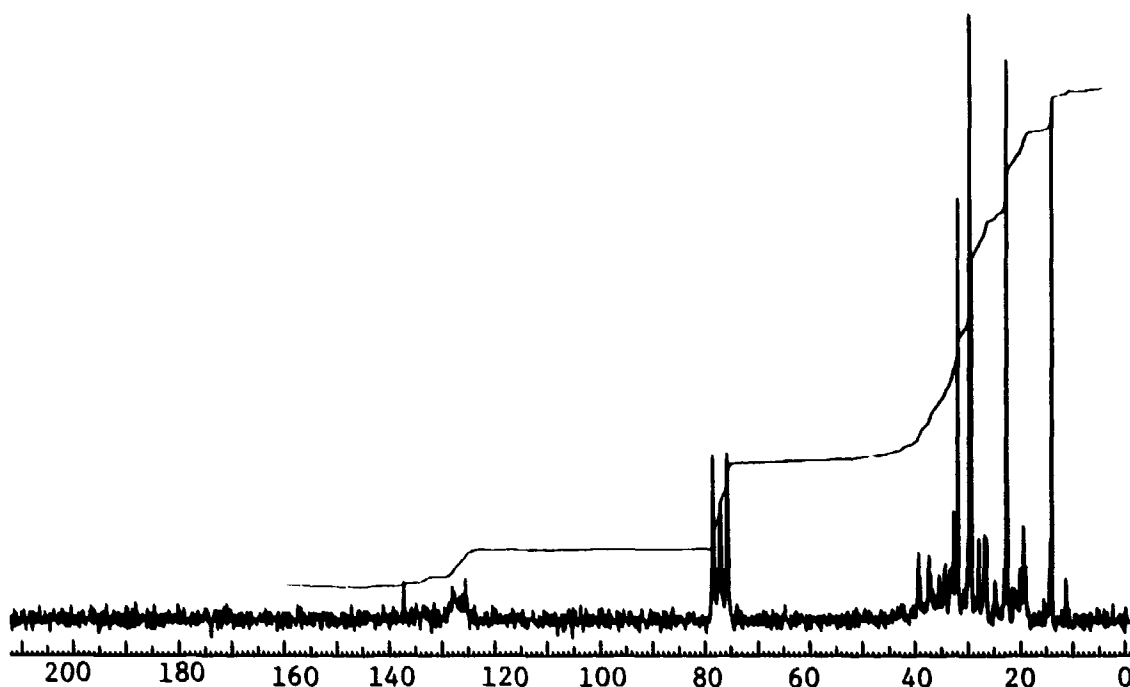
Figure A-12. ^{13}C NMR spectrum of JP-8 with NOE suppression
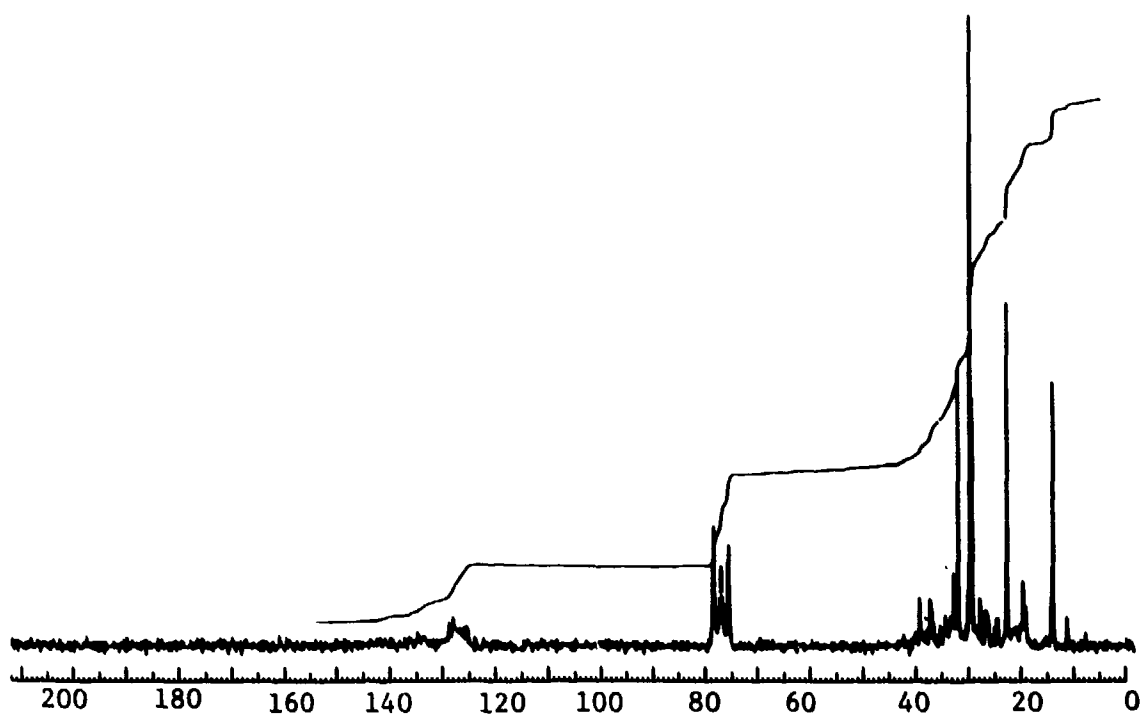
Figure A-13. ^{13}C NMR spectrum of DF-2 with NOE suppression

34
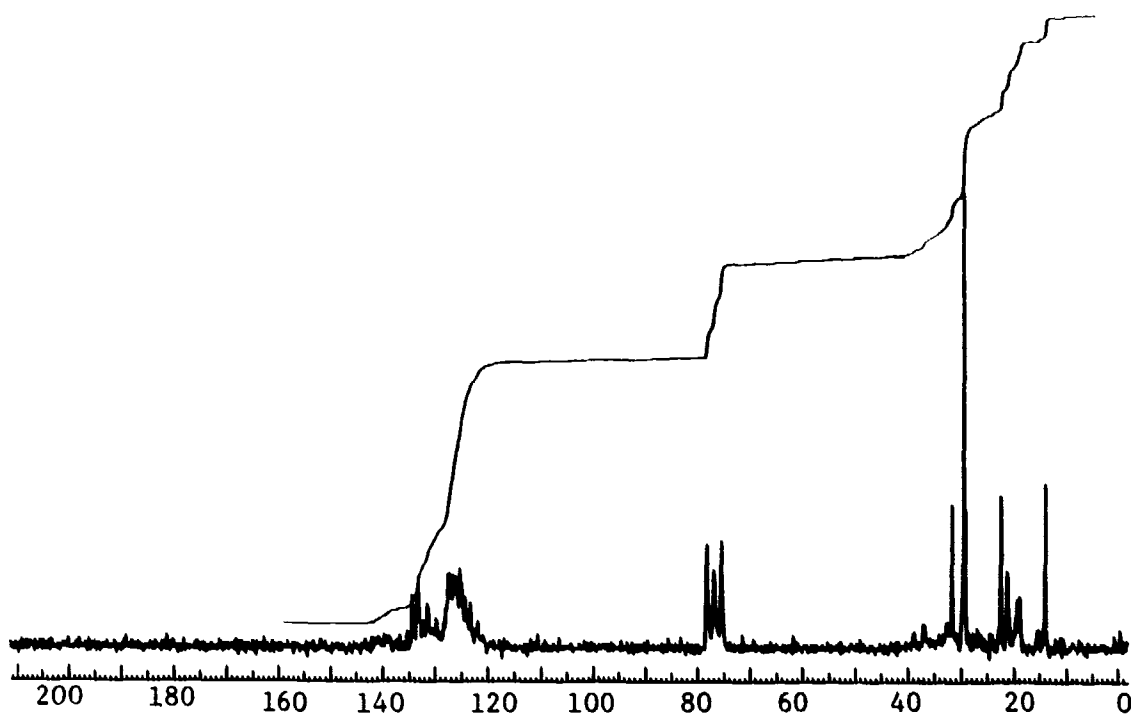
Figure A-14. ^{13}C NMR spectrum of light cycle oil with NOE suppression

Figure A-15. ^{13}C NMR spectrum of DF-1 with NOE suppression
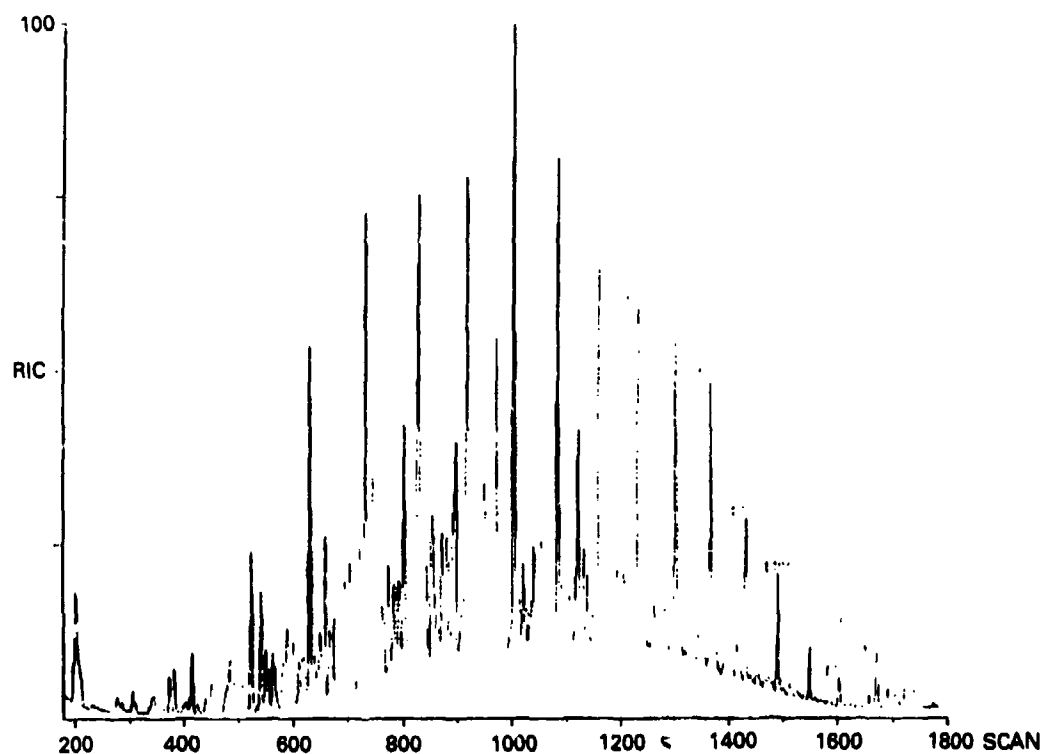
Figure A-16. GC chromatogram of JP-8

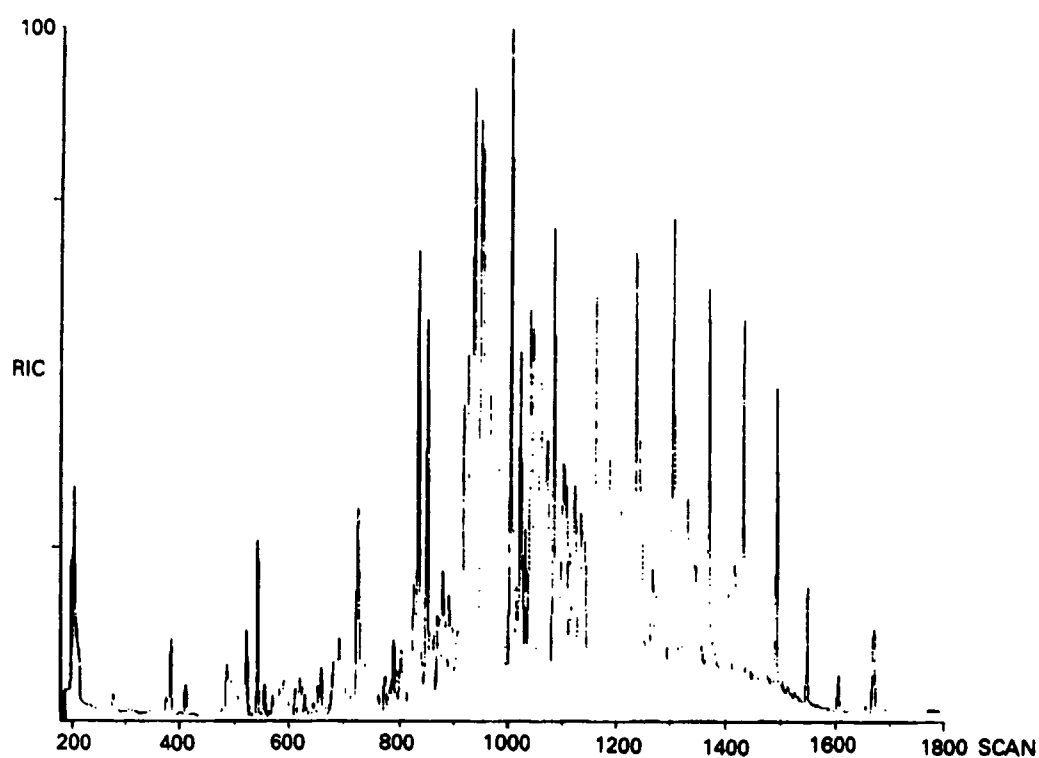Figure A-17. GC chromatogram of DF-2

36

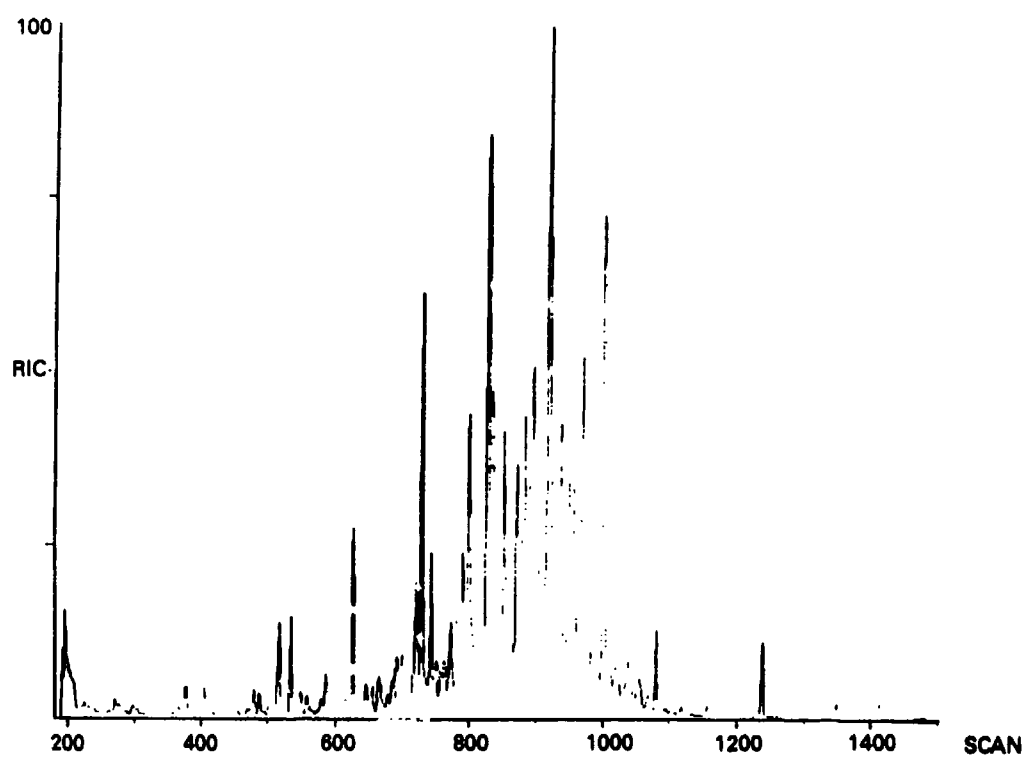Figure A-18. GC chromatogram of light cycle oil

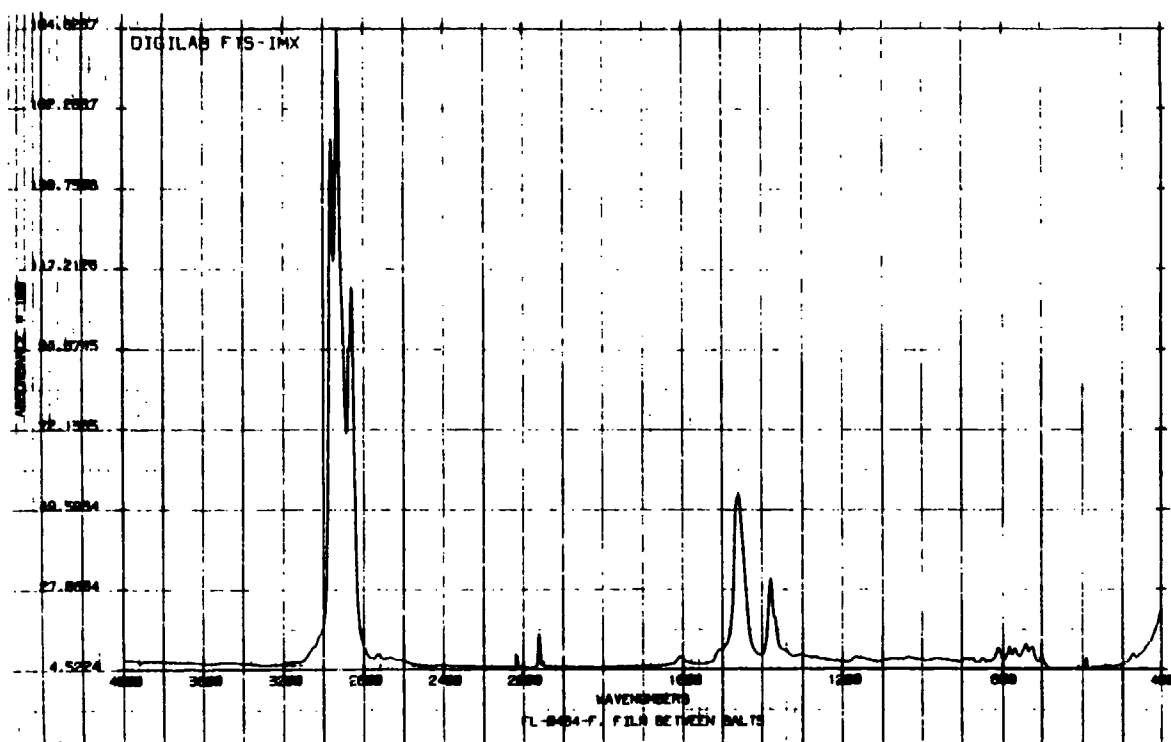Figure A-19. GC chromatogram of DF-1

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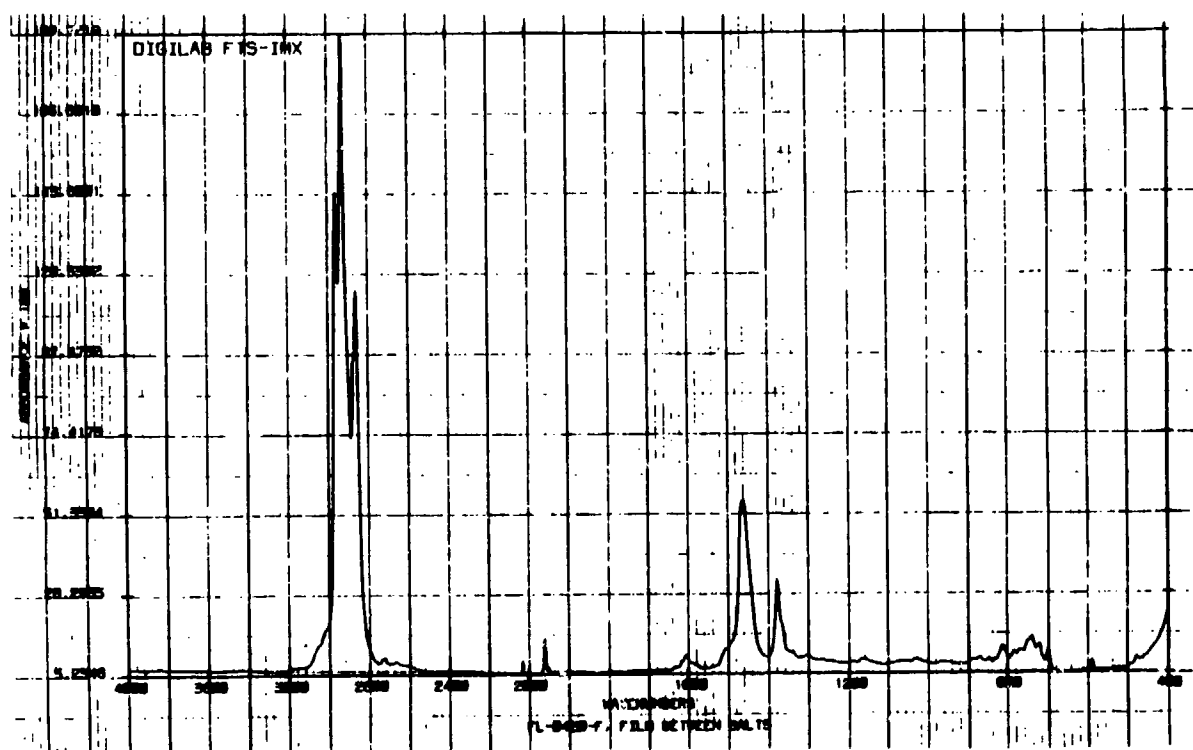Figure A-20. FTIR spectrum of JP-8
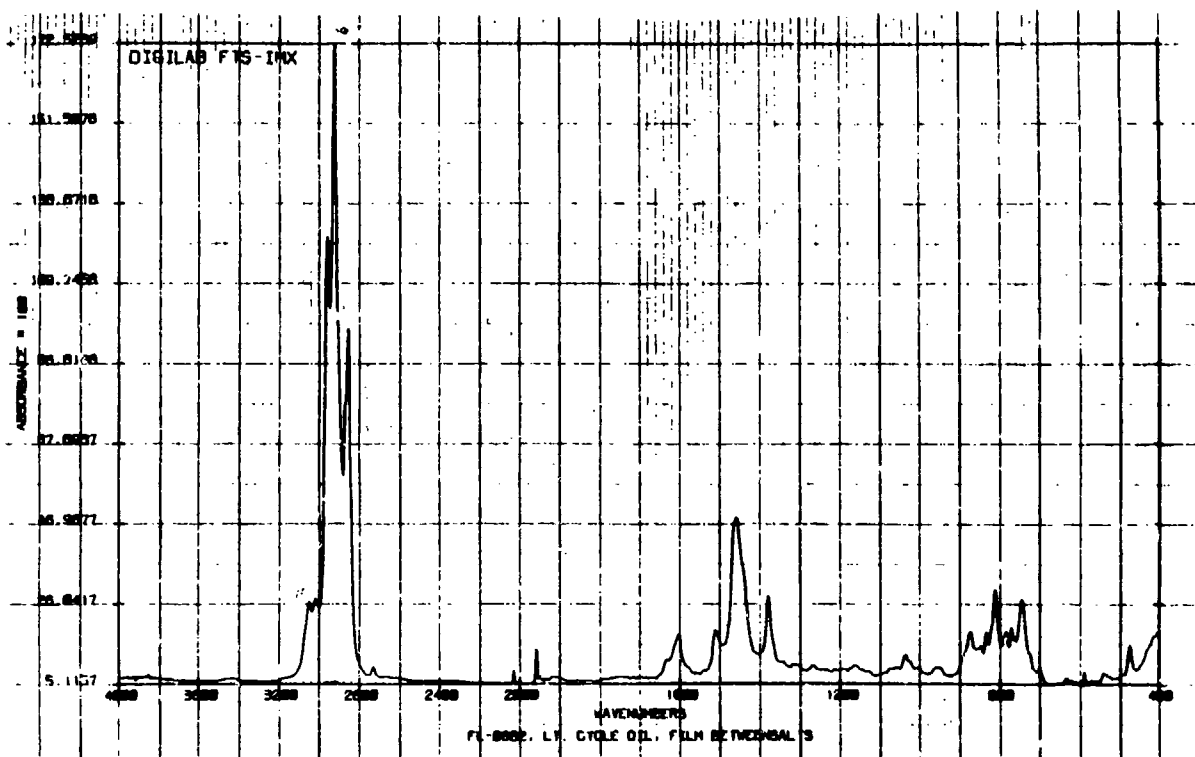

Figure A-21. FTIR spectrum of DF-2

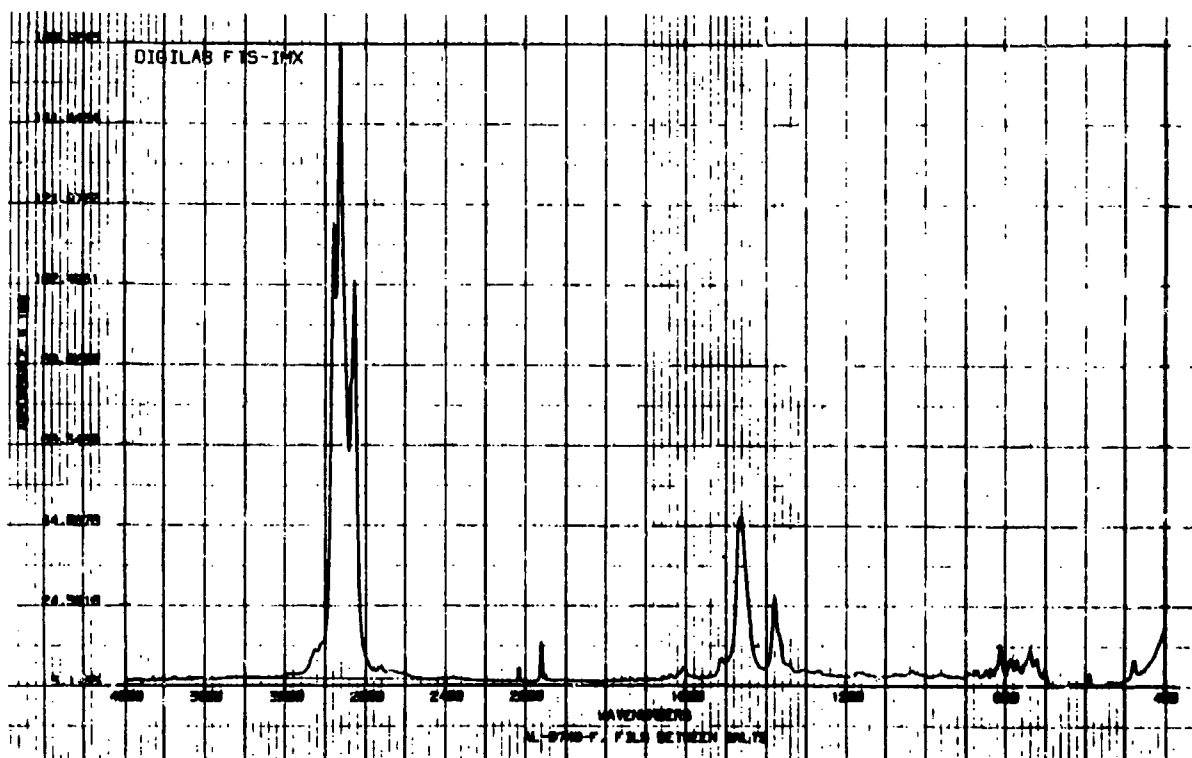Figure A-22. FTIR spectrum of light cycle oil

Figure A-23. FTIR spectrum of DF-1

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Figure A-24. GC chromatogram of DF-1, pyrolysis at 1000°C

Figure A-25. GC chromatogram of DF-1, pyrolysis at 700°C

Figure A-26. GC chromatogram of DF-1, pyrolysis at 350°C

Figure A-27. GC chromatogram of JP-8, pyrolysis at 1000°C

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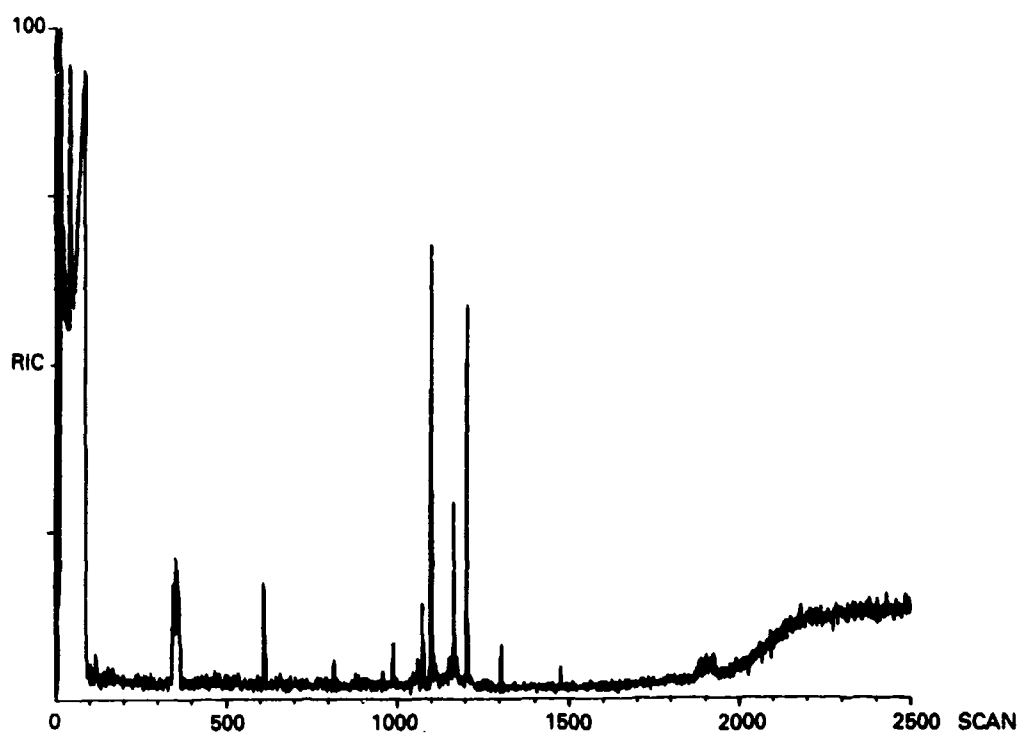Figure A-28. GC chromatogram of JP-8, pyrolysis at 700°C

Figure A-29. GC chromatogram of JP-8, pyrolysis at 350°C

Figure A-30. GC chromatogram of DF-2, pyrolysis at 1000°C

Figure A-31. GC chromatogram of DF-2, pyrolysis at 700°C

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Figure A-32. <u>GC chromatogram of DF-2, pyrolysis at 350°C</u>

Figure A-33. <u>GC chromatogram of light cycle oil, pyrolysis at 1000°C</u>

Figure A-34. GC chromatogram of light cycle oil, pyrolysis at 00°C

Figure A-35. GC chromatogram of light cycle oil, pyrolysis at 350°C
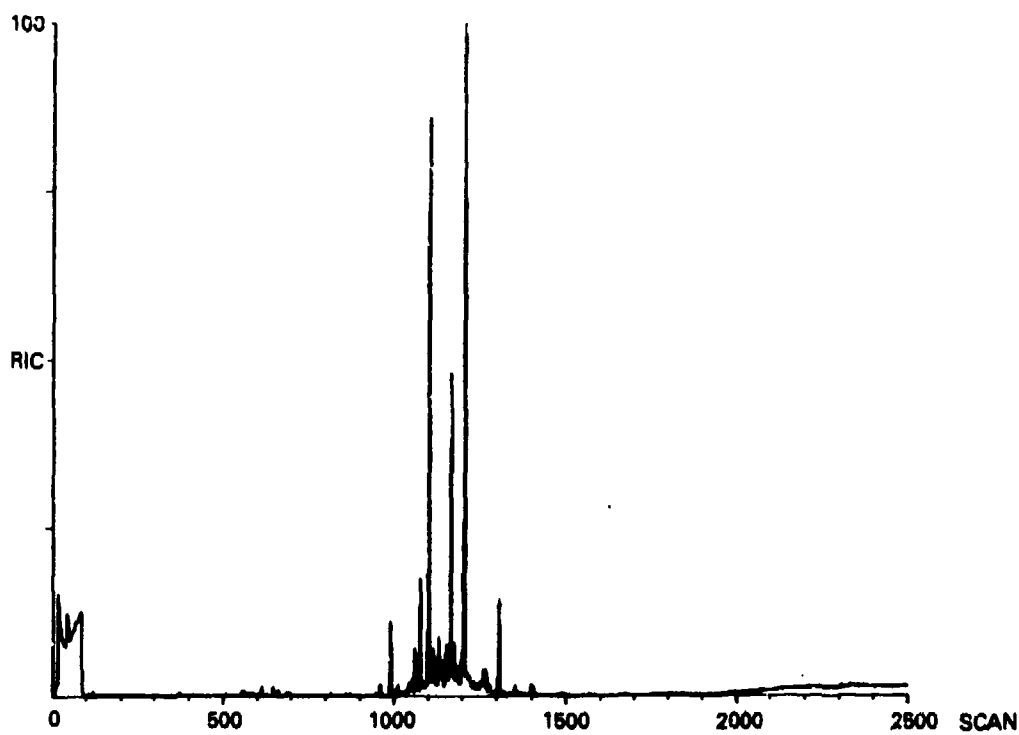
45

Figure A-36. <u>GC chromatogram of DF-1 SF, pyrolysis at 1000°C</u>
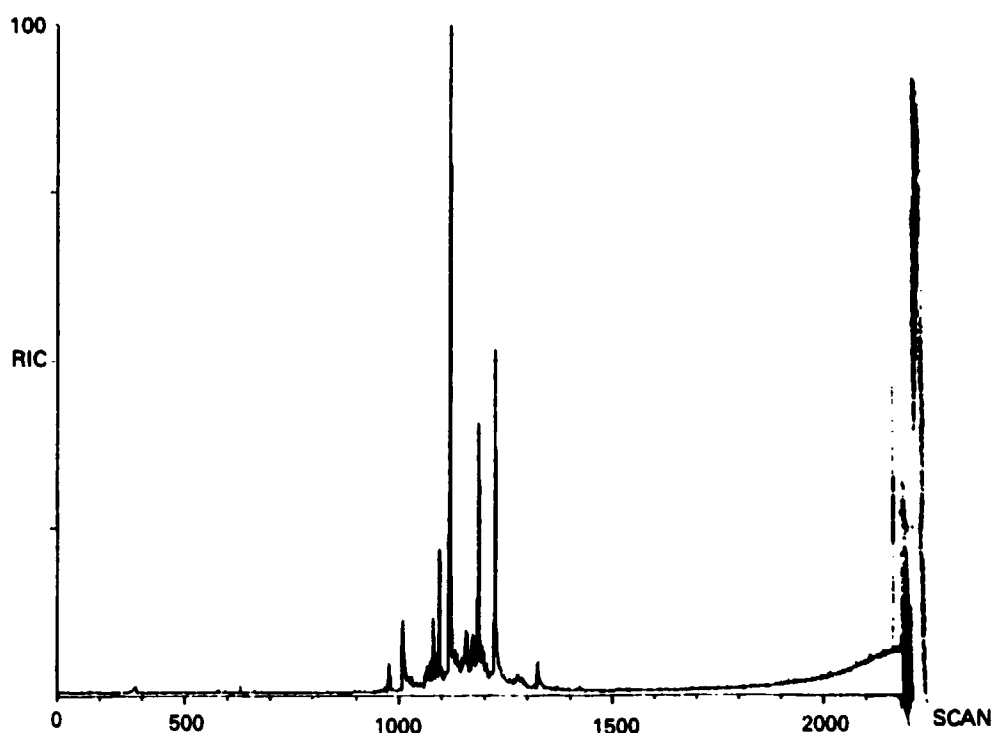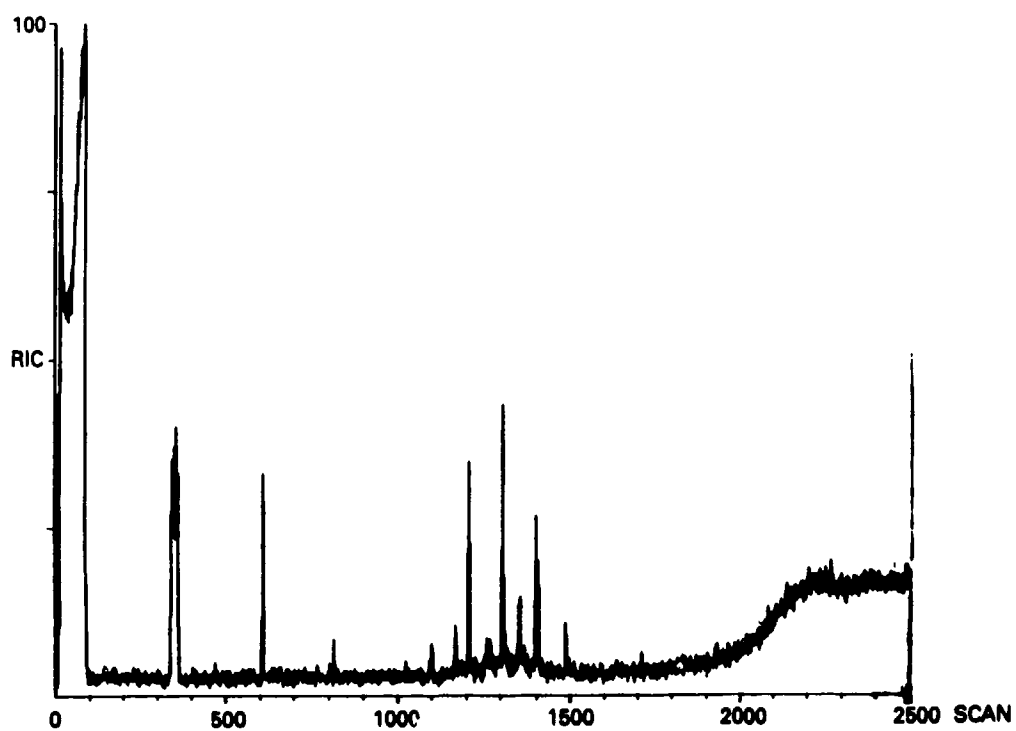

Figure 37. <u>GC chromatogram of DF-1 SF, pyrolysis at 350°C</u>

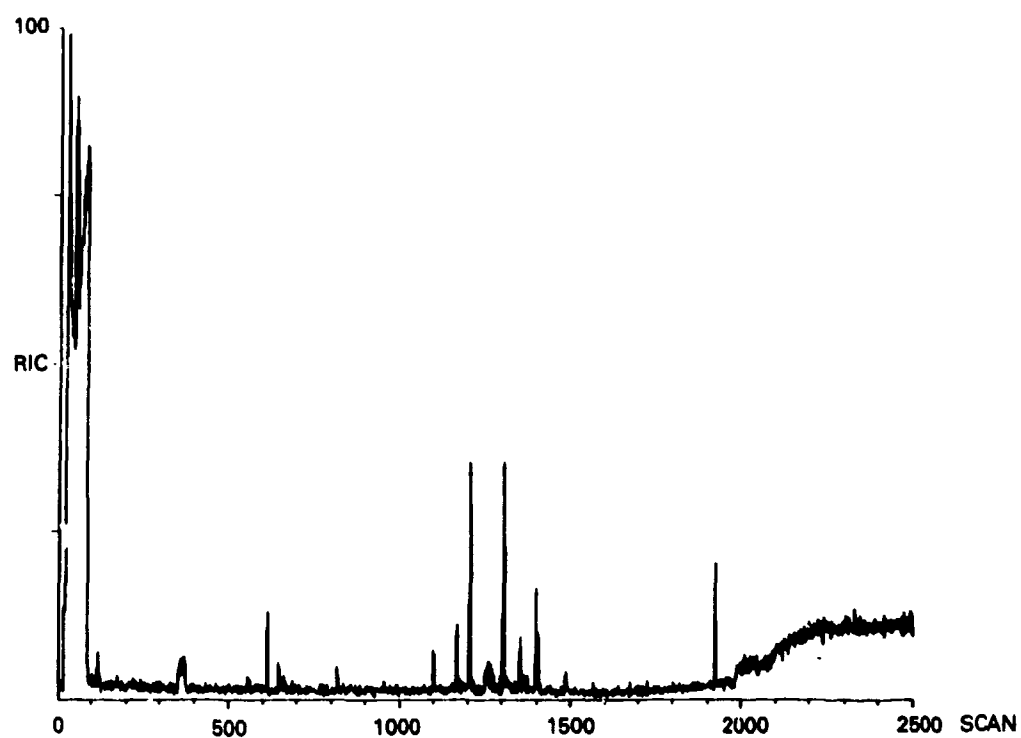Figure A-38. GC chromatogram of JP-8 SF, pyrolysis at 1000°C
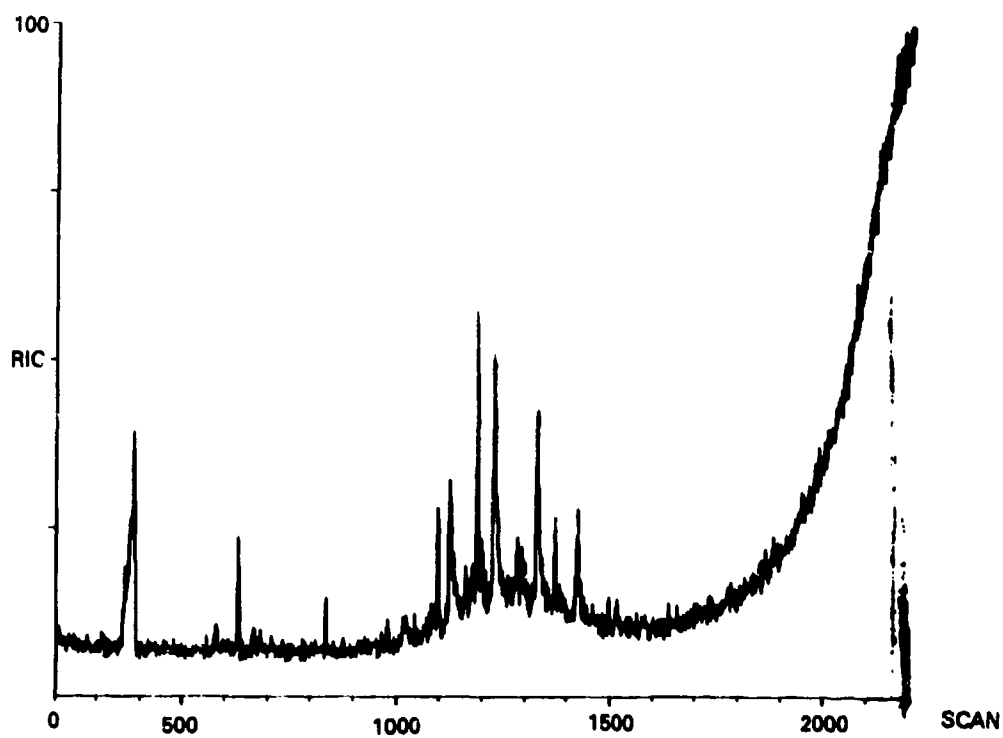

Figure A-39. GC chromatogram of JP-8 SF, pyrolysis at 350°C
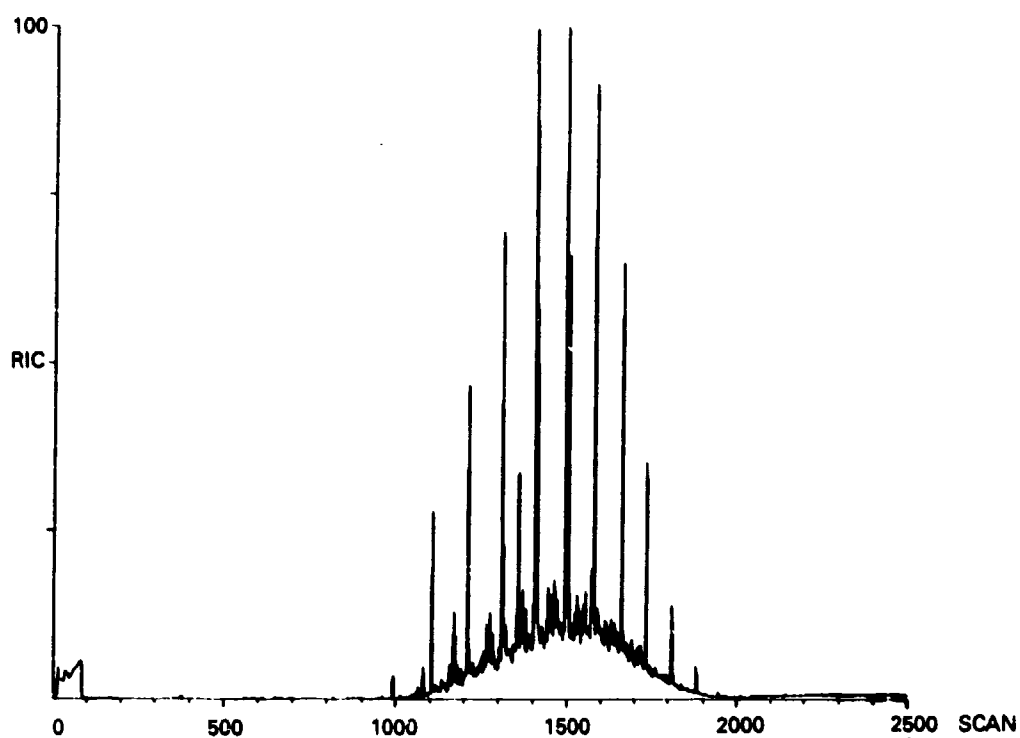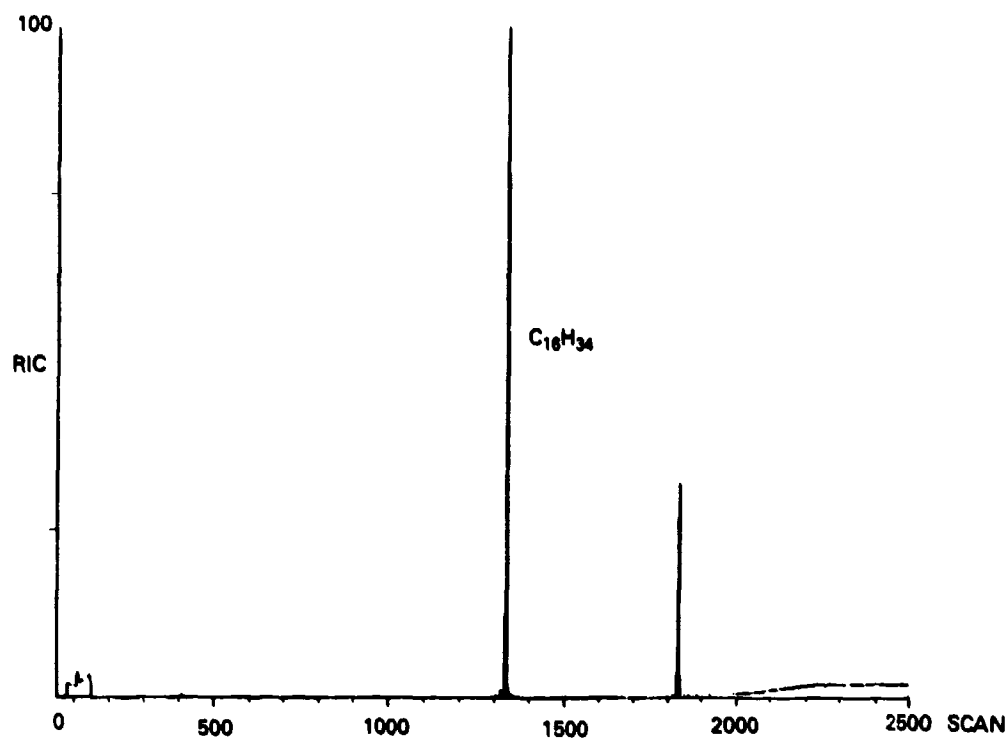
Figure A-40. **GC chromatogram of DF-2 SF, pyrolysis at 1000°C**
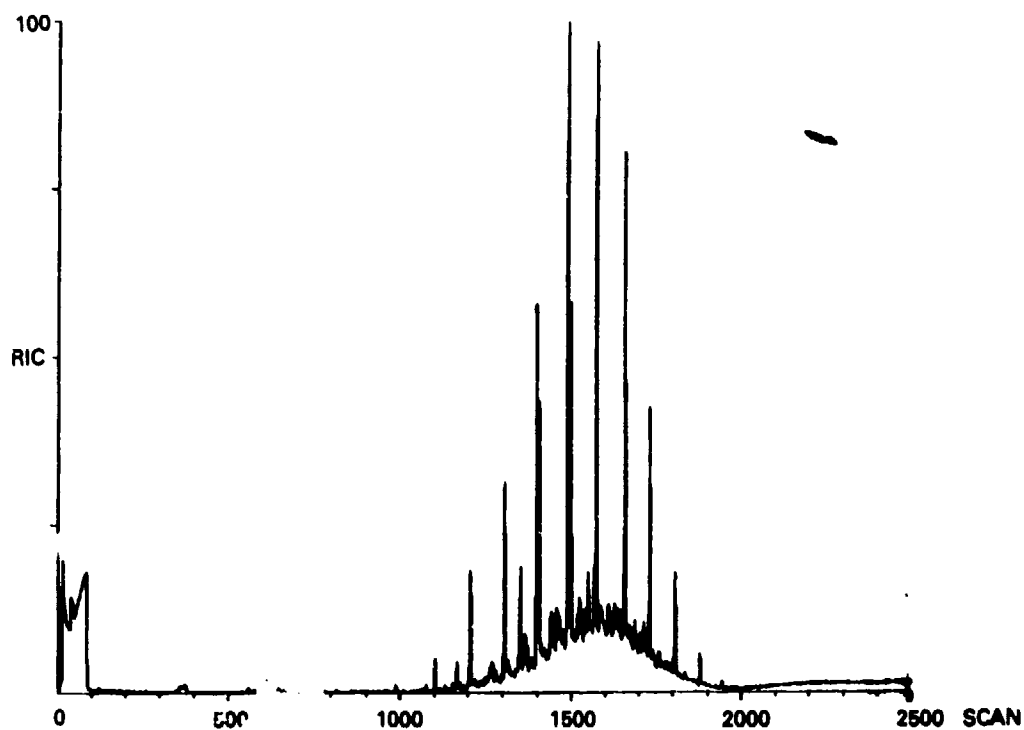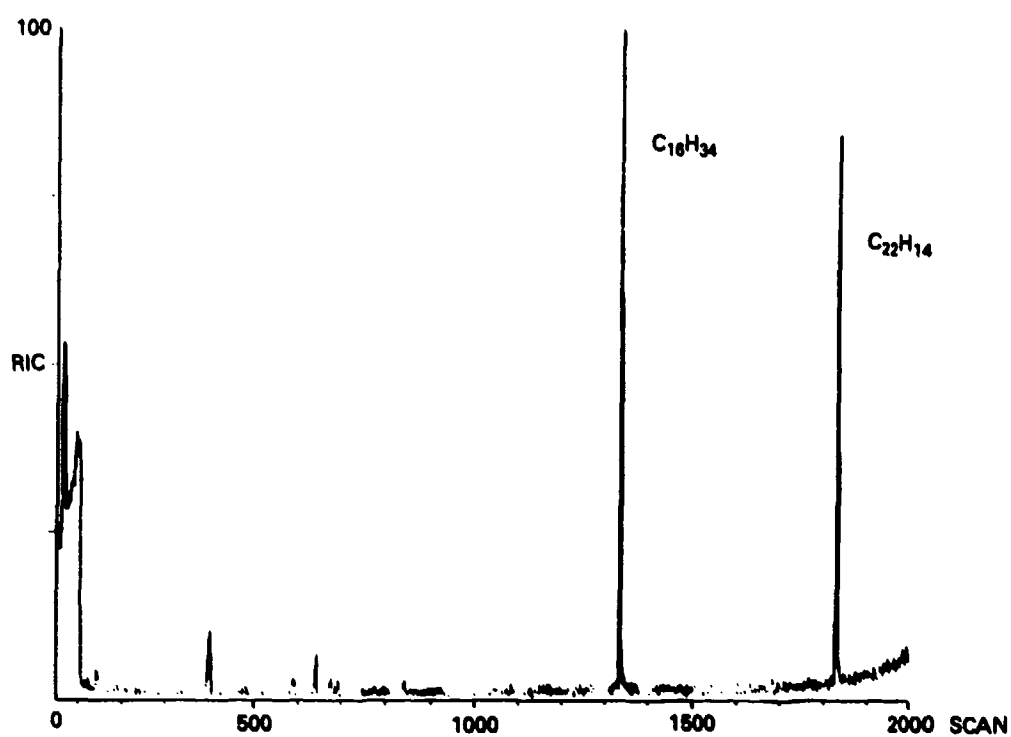

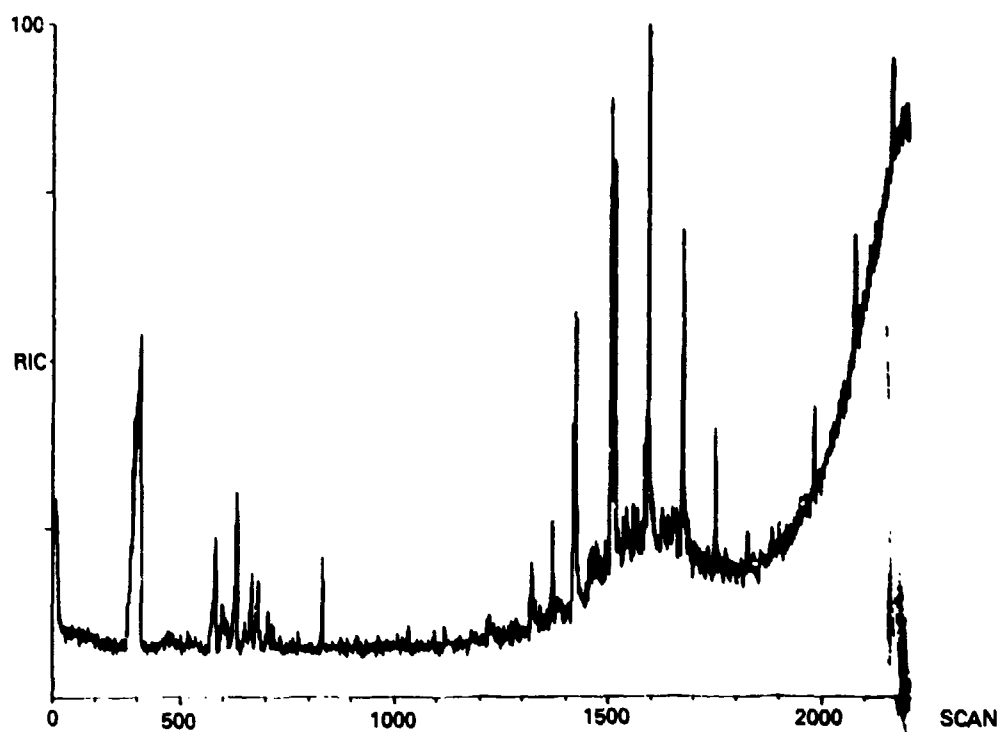Figure A-41. **GC chromatogram of DF-2 SF, pyrolysis at 350°C**
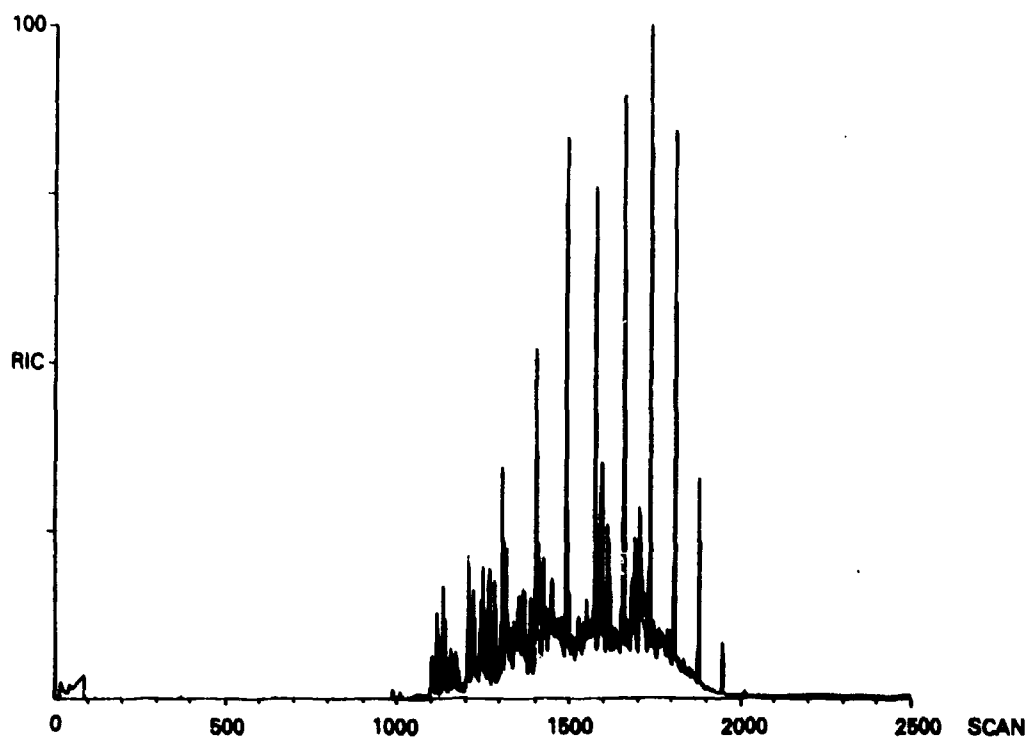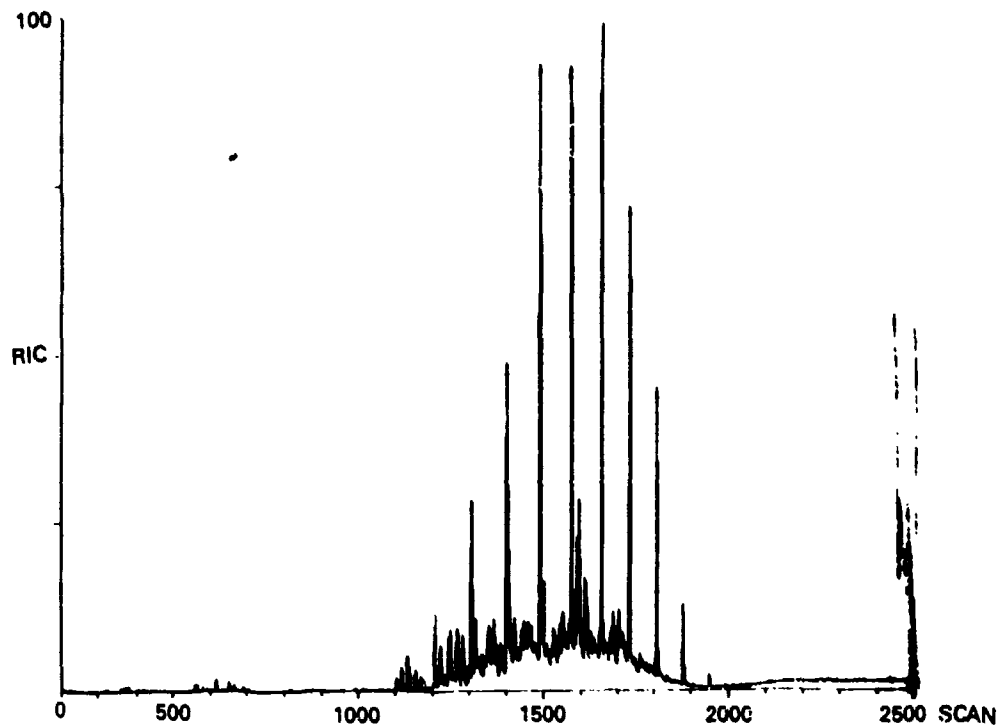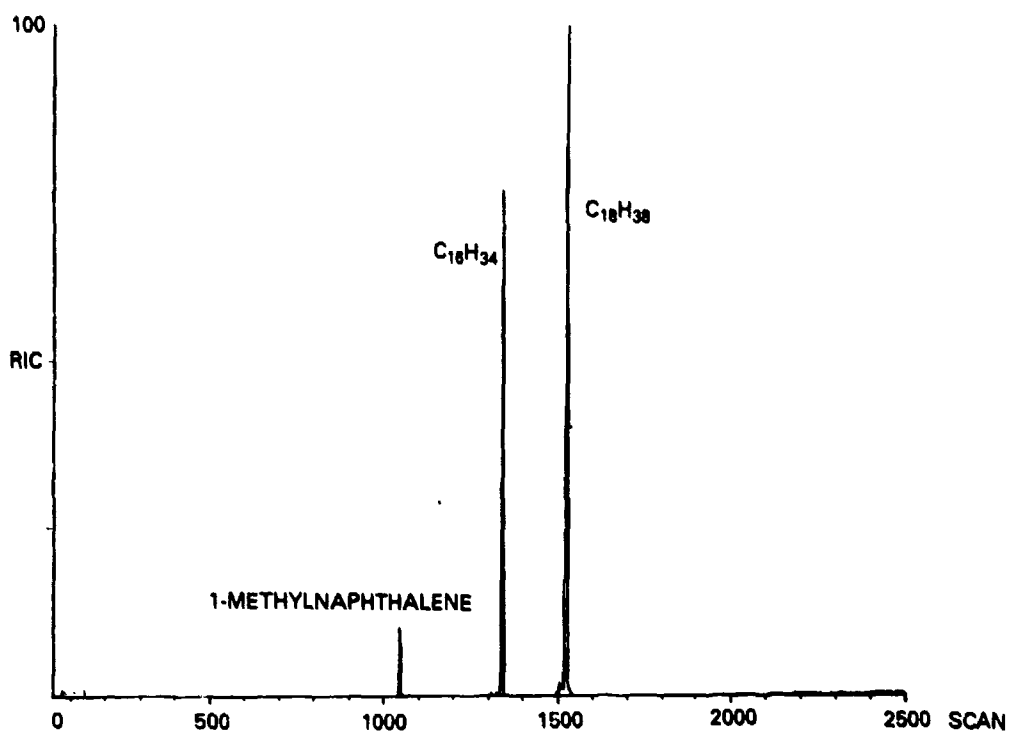
Figure A-42. GC chromatogram of light cycle oil SF, pyrolysis at 1000°C

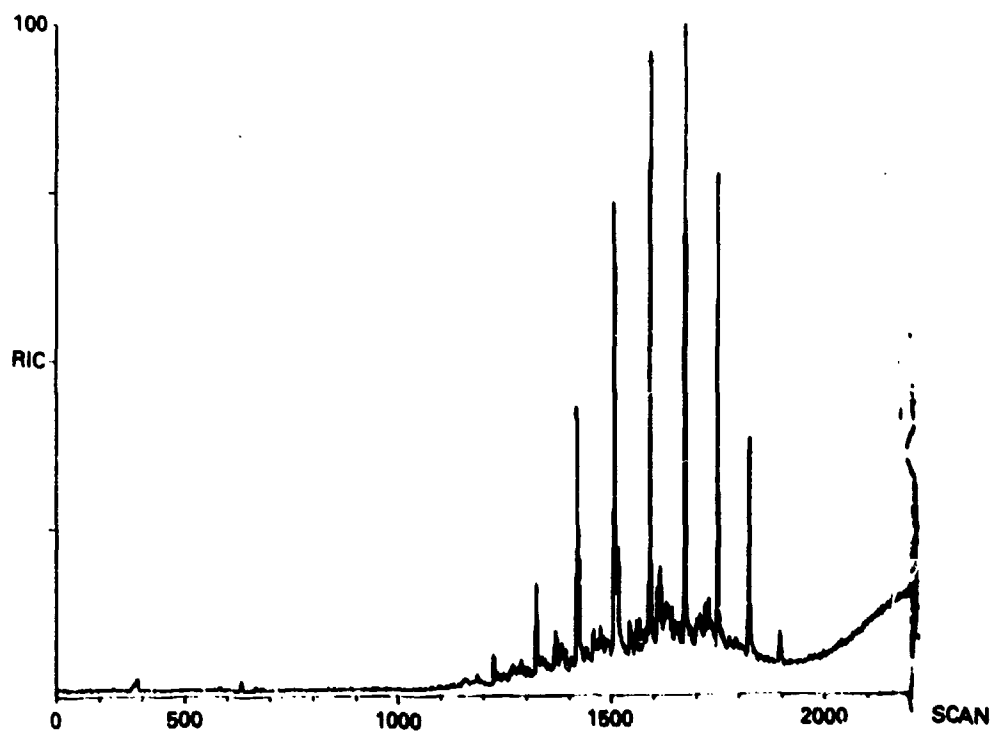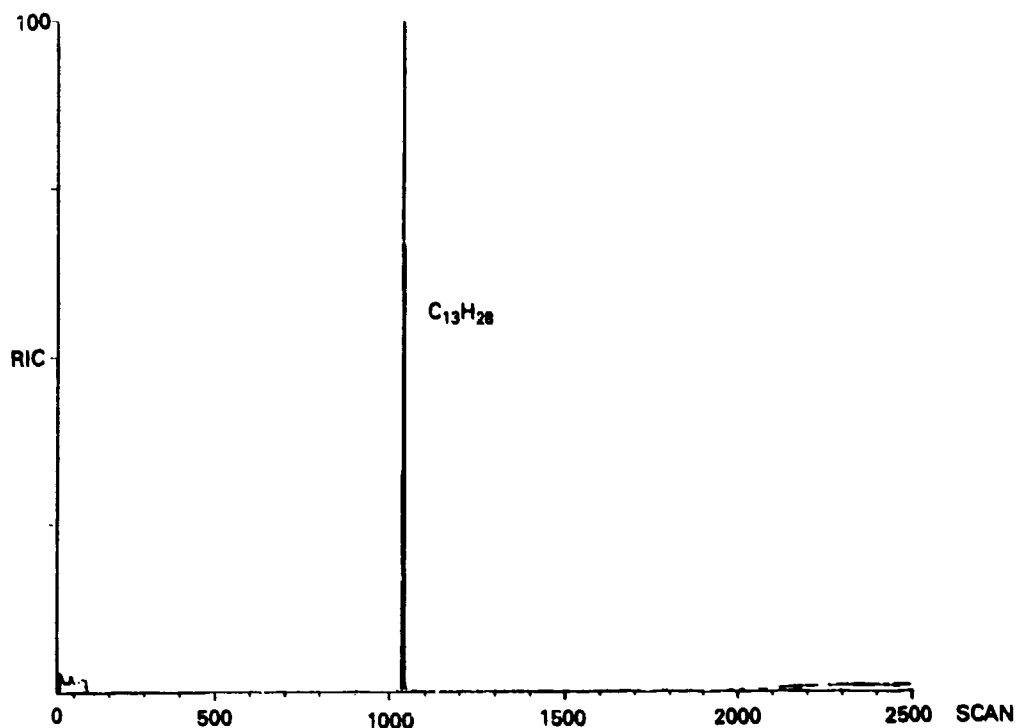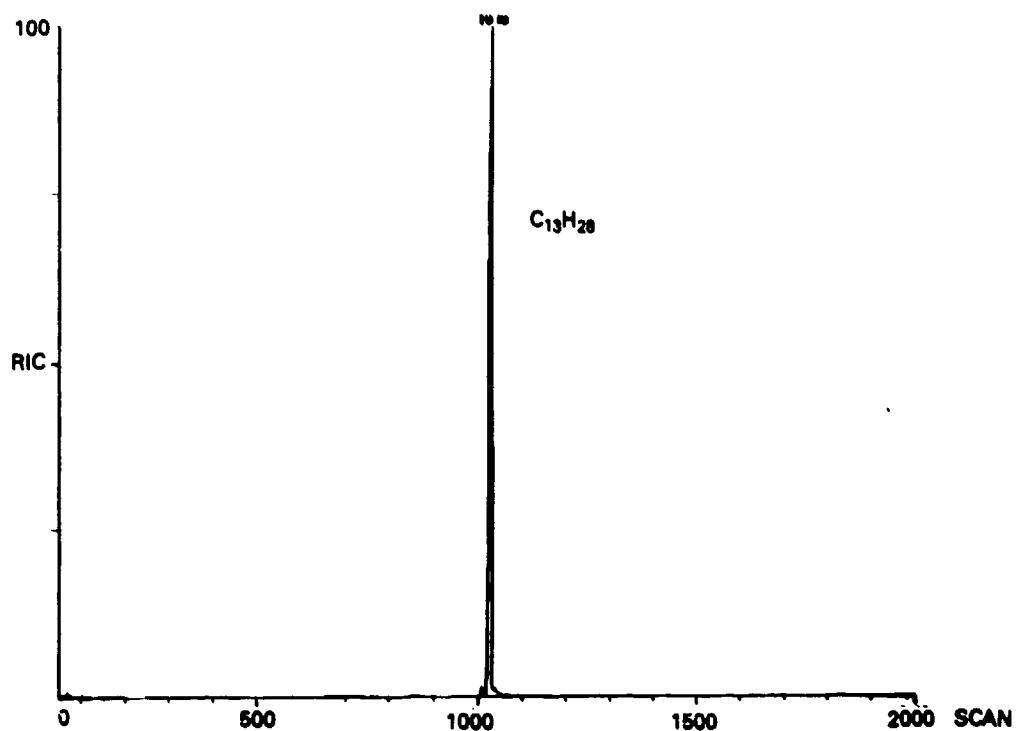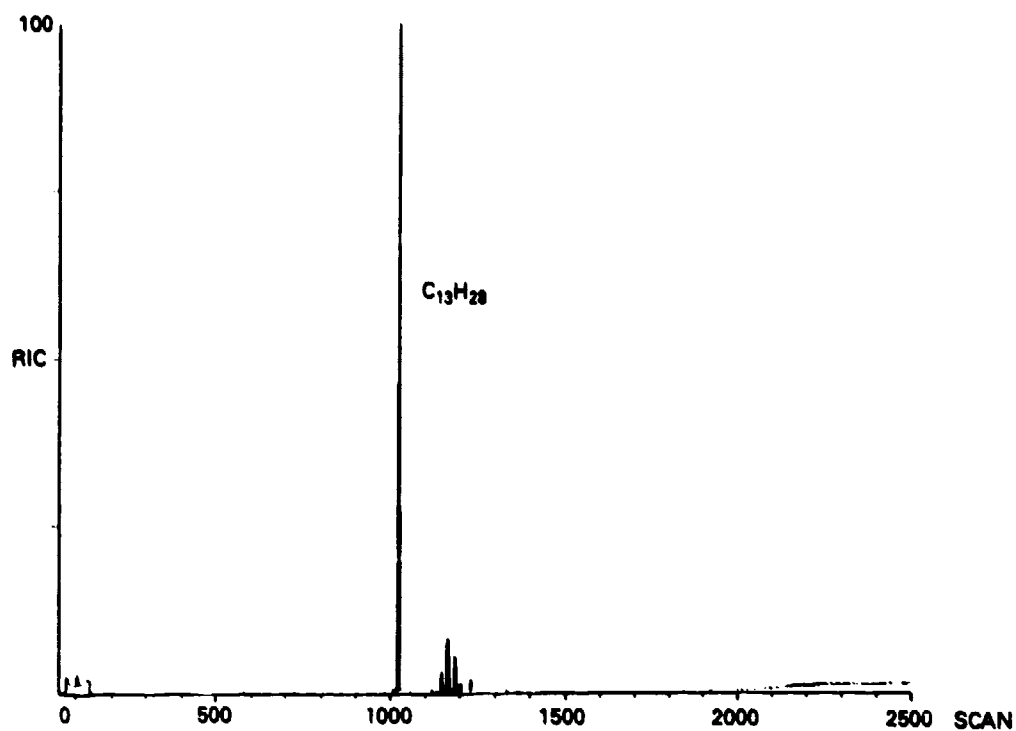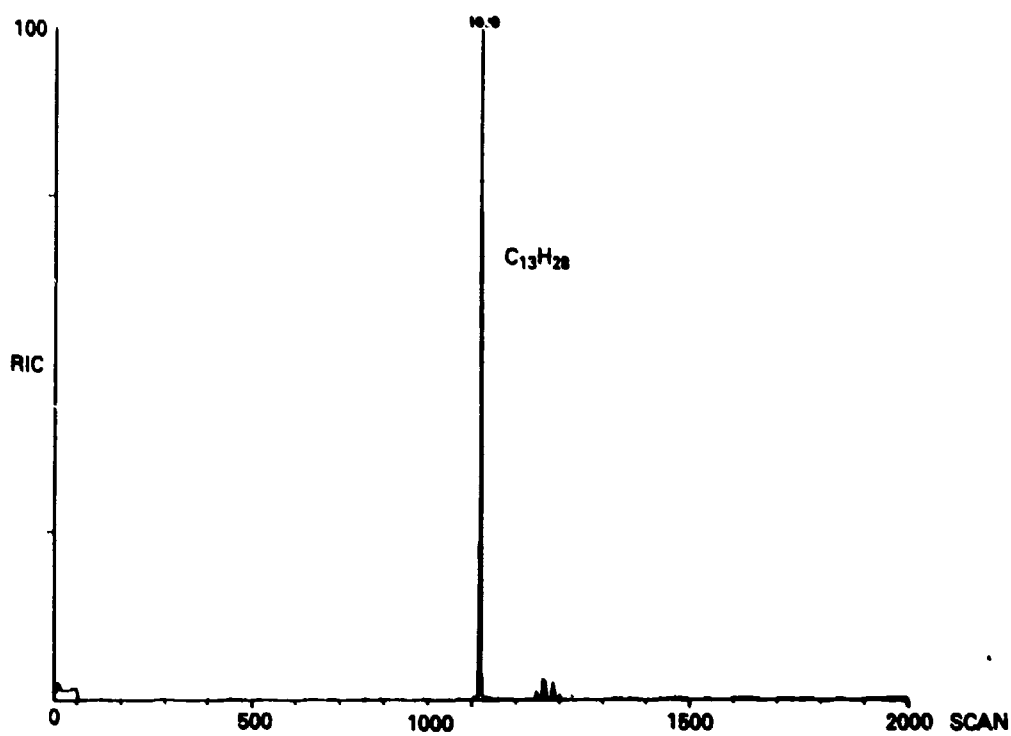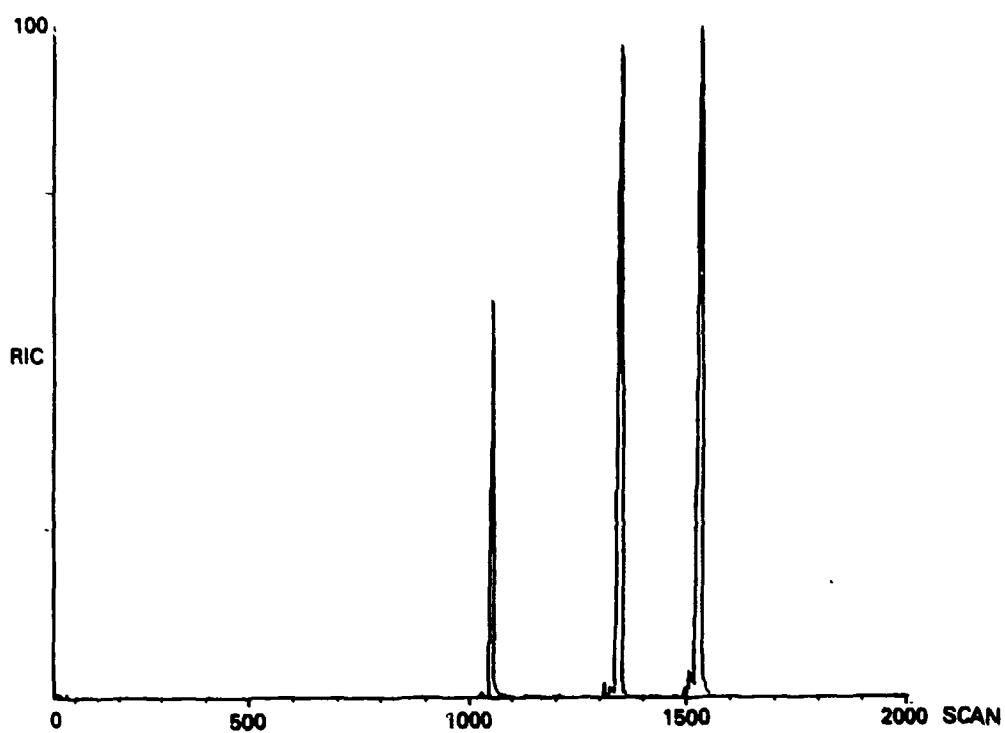**Figure A-43.** GC chromatogram of light cycle oil SF, pyrolysis at 350°C

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CDR
US ARMY ORDNANCE CENTER &
   SCHOOL
ATTN: ATSL-CD-CS   1
ABERDEEN PROVING GROUND MD
21005

CDR
AMC MATERIEL READINESS SUPPORT
   ACTIVITY (MRSA)
ATTN: AMXMD-MO (MR BROWN)   1
LEXINGTON KY 40511-5101

CDR
US ARMY FOREIGN SCIENCE & TECH
   CENTER
ATTN: AIAST-RA-ST3 (MR BUSI)   1
      AIAST-MT-1   1
FEDERAL BLDG
CHARLOTTESVILLE VA 22901

PROJECT MANAGER, LIGHT COMBAT
   VEHICLES
ATTN: AMCPM-LCV-TC   1
WARREN, MI 48397

HQ, US ARMY T&E COMMAND
ATTN: AMSTE-TO-O   1
      AMSTE-CM-R-O   1
      AMSTE-TE-T (MR RITONDO)   1
ABERDEEN PROVING GROUND MD
21005-5006

CDR
US ARMY ARMAMENT RESEARCH
   & DEVELOPMENT CTR
ATTN: AMSMC-LC   1
      AMSMC-SC   1
DOVER NJ 07801-5001

CDR, US ARMY TROOP SUPPORT
   COMMAND
ATTN: AMSTR-ME   1
      AMSTR-S   1
      AMSTR-E   1
      AMSTR-WL (MR BRADLEY)   1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
CONSTRUCTION ENG RSCH LAB
ATTN: CERL-EM   1
      CERL-ES (MR CASE)   1
      CERL-EH   1
P O BOX 4005
CHAMPAIGN IL 61820

TRADOC LIAISON OFFICE
ATTN: ATFE-LO-AV   1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
US ARMY NATICK RES & DEV CENTER
ATTN: STRNA-YE (DR KAPLAN)   1
      STRNA-U   1
NATICK MA 01760-5000

CDR
US ARMY QUARTERMASTER SCHOOL
ATTN: ATSM-CD   1
      ATSM-TD   1
      A: M-PFS (MR ELLIOTT)   1
FORT LEE VA 23801

HQ
US ARMY TRAINING & DOCTRINE CMD
ATTN: ATCD-SL-5   1
FORT MONROE VA 23651-5000

DIRECTOR
US ARMY RSCH & TECH ACTIVITIES
   (AVSCOM)
PROPULSION DIRECTORATE
ATTN: SAVDL-PL-D (MR ACURIO)   1
21000 BROOKPARK ROAD
CLEVELAND OH 44135-3127

CDR
US ARMY TRANSPORTATION SCHOOL
ATTN: ATSP-CD-MS (MR HARNET)   1
FORT EUSTIS VA 23604-5000

PROJ MGR, PATRIOT PROJ OFFICE
ATTN: AMCPM-MD-T-C   1
U.S. ARMY MISSILE COMMAND
REDSTONE ARSENAL AL 35898

HQ, US ARMY ARMOR CENTER AND
   FORT KNOX
ATTN: ATSB-CD   1
FORT KNOX KY 40121

CDR
101ST AIRBORNE DIV (AASLT)
ATTN: AFZB-KE-J   1
       AFSB-KE-DMMC   1
FORT CAMPBELL KY 42223

CDR
US ARMY WESTERN COMMAND
ATTN: APLG-TR   1
FORT SCHAFTER HI 96858

CDR
COMBINED ARMS COMBAT
   DEVELOPMENT ACTIVITY
ATTN: ATZL-CAT-E   1
       ATZL-CAT-A   1
FORT LEAVENWORTH KS 66027-5300

CDR
US ARMY LOGISTICS CTR
ATTN: ATCL-MS (MR A MARSHALL)   1
       ATCL-C   1
FORT LEE VA 23801-6000

PROJECT MANAGER
PETROLEUM & WATER LOGISTICS
ATTN: AMCPM-PWL   1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
US ARMY FIELD ARTILLERY SCHOOL
ATTN: ATSF-CD   1
FORT SILL OK 73503-5600

CDR
US ARMY ENGINEER SCHOOL
ATTN: ATZA-TSM-G   1
       ATZA-CD   1
FORT BELVOIR VA 22060-5606

CDR
US ARMY INFANTRY SCHOOL
ATTN: ATSH-CD-MS-M   1
FORT BENNING GA 31905-5400

DIR
US ARMY MATERIALS TECHNOLOGY
   LABORATORY
ATTN: SLCMT-M   1
       SLCMT-EM (DR FOPIANO)   1
WATERTOWN MA 02172-2796

CDR
US ARMY MISSILE CMD
ATTN: AMSMI-U   1
       AMSMI-RR   1
REDSTONE ARSENAL AL 35898-5242

CDR
US ARMY ARMOR & ENGINEER BOARD
ATTN: ATZK-AE-AR   1
       ATZK-AE-LT   1
FORT KNOX KY 40121

CDR
US ARMY MEDICAL BIOENGINEERING
   R&D LABORATORY
ATTN: SGRD-USG-M (MR EATON)   1
FORT DETRICK, MD 21701

CDR
US ARMY AVIATION CTR & FT RUCKER
ATTN: ATZQ-DI   1
FORT RUCKER AL 36362

PROG MGR, TANK SYSTEMS
ATTN: AMCPM-GCM-SM   1
       AMCPM-M60   1
WARREN MI 48397

CHIEF, U.S. ARMY LOGISTICS
ASSISTANCE OFFICE, FORSCOM
ATTN: AMXLA-FO (MR PITTMAN)   1
FT MCPHERSON GA 30330

CDR
US ARMY SAFETY CENTER
ATTN: PESC-SSD (MR BUCHAN)   1
FORT RUCKER AL 36362

DEPARTMENT OF THE NAVY

CDR
NAVAL AIR PROPULSION CENTER
ATTN: PE-33 (MR D'ORAZIO)   1
       PE-32 (MR MANGIONE)   1
P O BOX 7176
TRENTON NJ 06828

CDR
NAVAL SEA SYSTEMS CMD
ATTN: CODE 05M4   1
WASHINGTON DC 20362-5101

CDR
DAVID TAYLOR NAVAL SHIP R&D CTR
ATTN: CODE 2830 (MR SINGERMAN)   1
       CODE 2759 (MR STRUCKO)   1
       CODE 2831   1
ANNAPOLIS MD 21402-5067

PROJ MGR, M60 TANK DEVELOPMENT
ATTN: USMC-LNO   1
US ARMY TANK-AUTOMOTIVE
   COMMAND (TACOM)
WARREN MI 48397

DEPARTMENT OF THE NAVY
HQ, US MARINE CORPS
ATTN: LPP (MAJ LANG)   1
      LMM/2 (MAJ PATTERSON)   1
WASHINGTON DC 20380

CDR
NAVAL AIR SYSTEMS CMD
ATTN: CODE 53645 (MR MEARNS)   1
WASHINGTON DC 20361

CDR
NAVAL AIR DEVELOPMENT CTR
ATTN: CODE 60612   1
WARMINSTER PA 18974

CDR
NAVAL RESEARCH LABORATORY
ATTN: CODE 6170   1
      CODE 6180   1
      CODE 6110 (DR HARVEY)   1
WASHINGTON DC 20375-5000

CDR
NAVAL AIR ENGR CENTER
ATTN: CODE 92727   1
LAKEHURST NJ 08733

CDR
NAVAL FACILITIES ENGR CTR
ATTN: CODE 1202B (MR R BURRIS)   1
200 STOVAL ST
ALEXANDRIA VA 22322

COMMANDING GENERAL
US MARINE CORPS DEVELOPMENT
   & EDUCATION COMMAND
ATTN: DO74   1
QUANTICO VA 22134

OFFICE OF THE CHIEF OF NAVAL
   RESEARCH
ATTN: OCNR-126   1
      CODE 432 (DR MILLER)   1
ARLINGTON, VA 22217-5000

CHIEF OF NAVAL OPERATIONS
ATTN: OP 413   1
WASHINGTON DC 20350

CDR
NAVY PETROLEUM OFC
ATTN: CODE 43 (MR LONG)   1
CAMERON STATION
ALEXANDRIA VA 22304-6180

DEPARTMENT OF THE AIR FORCE

HQ, USAF
ATTN: LEYSF (COL LEE)   1
WASHINGTON DC 20330

HQ AIR FORCE SYSTEMS CMD
ATTN: AFSC/DLF   1
ANDREWS AFB MD 20334

CDR
US AIR FORCE WRIGHT AERONAUTICAL
   LAB
ATTN: AFWAL/POSF   1
      AFWAL/POSL (MR JONES)   1
      AFWAL/MLSE   1
      AFWAL/MLBT (MR SNYDER)   1
WRIGHT-PATTERSON AFB OH
45433-6563

CDR
WARNER ROBINS AIR LOGISTIC
   CTR
ATTN: WRALC/MMTV (MR GRAHAM)   1
ROBINS AFB GA 31098

CDR
SAN ANTONIO AIR LOGISTICS
   CTR
ATTN: SAALC/SFT (MR MAKRIS)   1
      SAALC/MMPRR   1
KELLY AIR FORCE BASE TX 78241

CDR
HQ 3RD USAF
ATTN: LGSF (CPT HEWITT)   1
APO NEW YORK 09127

OTHER GOVERNMENT AGENCIES

NATIONAL AERONAUTICS AND
   SPACE ADMINISTRATION   1
LEWIS RESEARCH CENTER
CLEVELAND OH 44135

DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION
ATTN: AWS-110   1
800 INDEPENDENCE AVE, SW
WASHINGTON DC 20590

US DEPARTMENT OF ENERGY
ATTN: MR ECKLUND   1
MAIL CODE CE-151
FORRESTAL BLDG.
1000 INDEPENDENCE AVE, SW
WASHINGTON DC 20585